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Workplace air — Quantitative determination of quartz and cristobalite in bulk materials by X-ray powder diffraction methods

WD stage

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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](https://www.iso.org/directives-and-policies.html)).

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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](https://www.iso.org/members.html).

Introduction

Exposure to Crystalline Silica (CS) in the respirable fraction of inhaled airborne dust is a hazard to the health of workers in many industries. For this standard, CS refers to the two most common polymorphs, quartz and cristobalite. To assess the exposure of an individual, personal samples of air are taken during a work activity, and then the amount of respirable CS is measured. In addition to the procedures for determining the airborne concentration of respirable CS in a workplace atmosphere, it can be useful, or required, to evaluate the CS content in bulk materials that have a potential risk of being respirable when they are ground or manipulated.

This document is appropriate to the analysis of material selected to be representative of a product, or soil, rock, mineral, waste, depending on the nature of the investigation. Bulk materials are generally in the solid state, but can also be made by watery mixtures of insoluble matter (slurries, muds). A variety of origins, compositions, sizes and shapes, such as solid blocks, fragments, slabs, sand, powders, and flours, can represent bulk materials.

The knowledge of CS content in natural rocks and soils is useful when, for example, assessing potential exposure by inhalation of airborne dust meeting the respirable convention of ISO 7708 [1] in work activities that involve excavation, earth moving, and drilling plant operations. Elevated exposures to respirable CS are often found in confined spaces, such as in mining and tunnelling. Knowing the weight fraction of CS in construction materials and natural rocks or soils contributes to the characterization of potential sources of airborne dust and allows planning of risk management measures in order to reduce potential exposures to airborne dust.

The methods in this document can also be used for the analysis of samples, which have been collected for the purpose of classification and labelling of chemicals according to the Globally Harmonized System (GHS), when a CS phase is found as a “substance”, or in “mixtures” and “articles”, as defined in the GHS.

As is necessary in any good routine type analysis, especially where the results may have legal implications, it is useful to establish standard procedures for analysing the specimens. There are several methods mentioned in the literature for the determination of quartz, and many procedures could be developed, but no single procedure is applicable to all situations. Standardizing procedures for X-Ray Powder Diffraction (XRPD) analysis of bulk materials, which are applicable to all materials, is difficult because of the variability of the matrices and their potential interferences. Therefore, the method chosen for the analysis should be carefully tested in the laboratory for the specific conditions.

The problems of processing samples containing quartz and/or cristobalite is essentially the same as processing samples of bulk materials in general, and the major problem is preparing a specimen that is representative of the bulk material. The potential accuracy obtainable from a sub-sample or specimen of bulk material is related to the effective number of particles interrogated by the X-ray beam, which is related to the distribution of particles sizes and their absorption coefficients.

Workplace air — Quantitative determination of quartz and cristobalite in bulk materials by X-ray powder diffraction methods

# Scope

This document specifies three methods for quantitative measurement of crystalline silica (CS) major polymorphs (quartz and cristobalite) weight percentage content in bulk samples using XRPD. General information is provided about their capabilities and limitations of relevance to laboratories working for routine testing.

Only X-ray diffractometers with Bragg-Brentano geometry are considered. The analysed specimen should be in the form of loose powder, where the median grain size is between 1 and 10 μm physical diameter. Block specimens are not considered.

Although a number of methods of analysis are considered in this document, other XRPD methods of analysis could be considered if demonstrated to give equivalent results.

# 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 14488, *Particulate materials — Sampling and sample splitting for the determination of particulate properties*

ISO 15767, *Workplace atmospheres — Controlling and characterizing uncertainty in weighing collected aerosols*

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

ISO 18158, *Workplace air — Terminology*

ISO 20581, *Workplace air — General requirements for the performance of procedures for the measurement of chemical agents*

EN 13925-1, *Non-destructive testing — X-ray diffraction from polycrystalline and amorphous material — Part 1: General principles*

EN 13925-2, *Non-destructive testing — X-ray diffraction from polycrystalline and amorphous material — Part 2: Procedures*

EN 13925-3, *Non-destructive testing — X-ray diffraction from polycrystalline and amorphous material — Part 3: Instruments*

# 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 terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at <https://www.iso.org/obp>

— IEC Electropedia: available at <http://www.electropedia.org/>

3.1

block

self-adhering single piece of interconnected particles or crystallites.

[SOURCE: EN 13925-1]

3.2

(bulk) sample

part of a defined bulk product taken for the purpose of characterization.

Note: While samples submitted for analysis may be immediately suitable for XRPD, it is more likely that the sample will require processing into a specimen prior to analysis.

[SOURCE: ISO 14488]

3.3

specimen

portion of the sample in the specific form used in the diffraction instrument for a given data collection process.

[SOURCE: EN 13925-1]

3.4

phase

portion of a physical system sharing a common molecular and inter-molecular structure irrespective of any subdivision by size distribution or shape.

Note: The term “phase” is used as a short form for a “crystallographic phase” or a “thermodynamic phase” throughout this document, unless explicitly stated otherwise.

[SOURCE: EN 13925-1]

3.5

diffraction line

region of the diffraction pattern containing an intensity maximum and corresponding to diffraction from a set of lattice planes.

Note: Often interchangeably referred to as a “peak”, “reflection” or “Bragg reflection”.

[SOURCE: EN 13925-1]

# Principle

The experimental technique used in this document to determine the diffraction pattern of a specimen is the “angular dispersive technique”, where the X-rays are monochromatic and the measurement is made by scanning the diffraction angle. Diffractometers with Bragg-Brentano geometry working in reflection geometry are to be used with this standard; transmission geometry is not considered.

Two types of powder specimens are considered in relation to their thickness:

* specimens of “infinite thickness”;
* “thin layer” specimens deposited on filters.

Note: “Infinite thickness” and “thin layer” are defined by the preparation steps in this document.

Phase identification is a preliminary step in every quantitative phase analysis and provides information necessary to a decision regarding the selection of procedure for quantitative analysis. The identification of both quartz and cristobalite in an unknown specimen by XRPD is based on visual or computer-assisted comparisons of portions of its X-ray powder pattern that should include at least two main peaks, compared to the experimental patterns of quartz and cristobalite reference materials.

Quantitative phase analysis - The percentages by mass of quartz and cristobalite are determined based on the integrated intensities of one or more individual diffraction lines of each phase. These intensities are compared to the corresponding values from calibration specimens. Three methods are considered:

- “External standard method” for thin layer specimens deposited on filters (comparison of the response obtained with the specimen to the response in a calibration line for quartz or cristobalite reference material, see 8.4.4);

- “Internal standard method”, for specimens of infinite thickness (addition of a known amount of a crystalline phase material that has been shown not present in the original sample, see 8.4.5);

- “Spiking method”, also called “standard addition method”, for specimens of infinite thickness and quartz contents below approximately 20%, depending on the matrix (addition of a known amount of quartz or cristobalite to the sample being studied, see 8.4.6).

Multiple methods applied to a single sample can be used to verify analyses. Whole powder pattern analysis and standard free methods (e.g. the Rietveld method) are not considered in this document.

# Equipment

## Diffraction system

### Diffractometer

This document has been prepared to be used with a diffractometer employing the Bragg-Brentano parafocusing geometry, where the specimen and the receiving slit all lay on the focusing circle. The vertical θ:θ or θ:2θ configurations are most advantageous for handling powder specimens. A diffractometer generally comprises:

- goniometer;

- X-ray source that includes the line-voltage supply, the high-voltage generator, and the X-ray tube. A conventional X-ray sealed tube source is often used, and the most commonly used tube anode material is copper;

- incident beam optics, that may include monochromatisation or filtering, collimation and/or focusing or parallelism of the beam;

- specimen stage; the specimen is contained in a specimen holder, which is constructed to allow specimen rotation around the appropriate axis;

- diffracted beam optics, that may include monochromatisation or filtering, collimation and/or focusing or parallelism of the beam;

- detector;

- data collection system.

Procedures for instrument alignment and performance characterisation of Bragg-Brentano diffractometers are given in EN 13925-3.

### Specimen holders

Several types of specimen holders can be used for diffraction analysis. The following standard circular specimen holders are recommended when the analytical methods described in this document are used.

- Specimen holder for loose powder with cavity mount; top, back or side loaded. For back-loading of powder, a specimen holder consists of a bottom plate, which supports the powder, and a ring. The diameter of the cavity to be filled generally varies between 15 mm and 30 mm, and the powder thickness is a minimum of 1 mm (for infinite thickness specimen).

- Specimen holder for 25-mm filter (for thin layer specimen), where the support base of the filter, or the filter itself, is a disc made of a metal (e.g. silver, zinc or aluminium).

## Balance

A microbalance capable of weighing ±1 μg or better over the range 0 g to 5 g is required for the preparation of specimens deposited on 25-mm filters (thin layer). For the preparation of specimens of infinite thickness, by mixing of powders, the materials should be weighed in glass weighing bottles with lids; capacities of 5-15 mL are generally required, so that the total weight exceeds 5 g, therefore, the balance operational range should span up to 20 g, and an analytical sensitivity of 10 μg will be sufficient. An electrostatic eliminator is needed when weighing.

## Reference materials

### Quartz and cristobalite

Pure quartz and cristobalite reference materials with a median size of particles in the range 1-10 μm, preferably smaller than 5 μm, and similar to the median size of particles in the specimens, are to be used. Reference materials can be prepared in the laboratory from pure quartz and cristobalite crystals, if the correct particle size is achieved and phase purity is characterized.

Note: United States National Institute of Science and Technology (NIST) have developed Standard Reference Materials (SRM’s) for respirable quartz (1878 series) and respirable cristobalite (1879 series) with certified phase purity.

### Internal standard

For the internal standard method, the chosen mineral phase should have a fully resolved diffraction line, not overlapping any lines of the CS phases, and free from microabsorption (i.e., be of very small particle size or have an absorption similar to the specimen) and extinction. Hence, it is essential that internal standard powder crystallite size be in the range 1-10 μm, preferably smaller than 5 μm, and similar to the median size of particles in the specimens. Internal standard, quartz, and cristobalite reference materials are generally prepared in the laboratory from pure crystals milled until the optimum size range is reached. A sufficient amount of each reference material should be prepared, tested, stored, and added to the specimens for analyses.

Note 1: The definition of “fully resolved” line is beyond the scope of this document. The experience of the analyst should guide in assessing and addressing this aspect of the analysis.

Note 2: Grain size may be measured by using one of the techniques described in section 7.3, Note 4, and purity characterized by XRPD.

Note 3: Corundum is a mineral phase often used as internal standard. NIST SRM 676a is a corundum structure-alumina powder intended primarily for use as an internal standard for quantitative determinations by XRPD.

### XRD drift correction disc

An aluminium or silicon polycrystalline disc, or other suitable robust material, should be used to correct for the drift in XRD radiation intensity over time.

Note: The sintered alumina disc NIST SRM 1976b is frequently used.

## Equipment for the preparation of specimens of infinite thickness

### Laboratory drying oven

For ovens of the forced-draft type, the air circulation should not be so strong that any transport of particles can take place.

### Masonry hammer, jaw crusher or similar device

Initial processing is often needed to reduce the material to the required size for milling. Fractionation (e.g. use of a masonry hammer or jaw crusher), of the material into smaller pieces can be performed dry, although, processing involving a grinding rather than a crushing action should be performed ‘wet’ to reduce the potential for a deterioration of crystalline structure.

### Laboratory mill

Several types of mechanical grinding devices, driven by a motor, can produce the required grinding action by freely moving milling pieces (i.e., balls and rods) in a cylindrical grinding chamber completely encapsulated. The device rotates at a given speed, and size reduction is achieved by impact and shear between the milling pieces, whose effectiveness is improved by vibration. Chamber and milling pieces made of the same material should be used. Hard materials such as tungsten carbide, silicon nitride, zirconium oxide, and corundum are recommended, while agate should be avoided because of potential contamination. Grinding chambers can typically have volumes between 80 and 500 mL, and the material filling can generally range between 15% and 50% of the volume (the instruction of the manufacturer should be followed). A so-called “micronizing” mill may also be used. This mill generally uses corundum cylindrical grinding elements in a small airtight polypropylene jar that handle a sample volume of 4 mL (or 10 g). Wet grinding (water, 2-propanol, or cyclohexane) is the preferred grinding method for a micronizing mill.

Note: The minimum quantity of material that can be ground is an important parameter. For example, if a 250 mL grinding chamber is used, a minimum filling of 30 mL is generally suggested. This minimum volume corresponds to a weight of approximately 40 g for a fine sand sample of average density (2,6 g cm-3). Therefore, if the sample weight is less than 40 g, it cannot be ground in the described chamber.

### Other equipment

Mortar and pestle - For hand grinding and mixing. They are manufactured out of many different materials, but hard mortar types such as boron carbide, are recommended, while agate might introduce contamination and should be avoided.

Preparation kit for mounting the powder in the specimen holder - The kit generally comprises a specimen “preparation table” onto which a specimen holder ring is clamped, a powder press block, and a spatula to remove the surplus powder (see 7.6).

Stainless steel test sieves - Used to verify fragments size before grinding them in the laboratory mill; a receiving pan is used to collect the passing material.

Note: Fragment sizes of less than 10 mm can generally be milled, but a smaller initial size improves the result of grinding. The use of a test sieve with aperture size between 2,0-2,8 mm is suggested when a ball or rod mill is used. If a “micronizing” mill is used, the sample may be passed through a 0,4 mm aperture sieve prior to grinding.

## Equipment for the preparation of thin thickness specimens

### Filters for analysis

Filters shall be of a 25 mm diameter. The filter types generally used for the XRPD analysis of CS, and their advantages and disadvantages, are listed in Table 1. These filter materials generally do not interfere with the measurement of the major reflections of quartz (101), (100), and (112), and cristobalite (101), (200 and 112), and (102). In any case, batches of filters should be tested to detect potential interferences, because impurities can be introduced during the filter manufacturing process. These tests are also useful to verify the background fluctuation levels, since they have an effect on the readability of diffraction peaks, worsening the limit of detection for CS. Silver filters exhibit the least variability and lowest background levels and thus are useful in situations where low limits of detection are required. However, cristobalite combined reflections (200 and 112) can sometimes be difficult to measure because they are located in the tail at the side of silver reflection (100). Silver and mixed esters of cellulose filters are rigid and easy to handle when weighing and loading in the sample holder. PVC and especially polycarbonate filters are flexible and require careful handling. A silver filter used for analysis allows an effective correction for absorption (see 8.4.4.3). When an organic filter with high or medium transparency to X-ray radiation (Table 1) is used for analysis, an effective correction for absorption can still be carried out by measuring the intensity of a reflection of the underlying metallic (e.g. silver, zinc or aluminium) support base.

**Table 1 — Examples of filters for CS analysis**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Filter material  pore size d | Interfering peaks | | | | | | Background Fluctuation Index a | | Mass absorption correction |
| Quartz | | | Cristobalite | | | Quartz | | Filter Transparency Index b |
| 101 | 100 | 112 | 101 | 200 | 102 | 101 | 100 |
| Silver  (Ag)  0,45 μm | no | no | no | no | yes | no | 1 | 1 | 1 |
| Polyvinyl chloride  (PVC)  5 μm | no | no | no | no | yes c | no | 1,5 | 1 | 0,72 |
| Mixed Esters of Cellulose  (MCE)  0,8 μm | no | no | no | no | yes c | no | 2,4 | 1,7 | 0,78 |
| Polycarbonate  (PC)  0,4 μm | no | no | no | no | yes c | no | 1,3 | 2,2 | 0,98 |
| Polytetrafluoroethylene  (PTFE)  0,5 μm | no | yes | no | yes | yes c | no | 2,5 | N.D. | 0,74 |
| a Background Fluctuation Index where and are the standard deviations of XRD intensities measured in the ranges of primary (Qz1) and secondary (Qz2) quartz peak profiles (Cu anode) on a blank silver filter, and on a blank filter of the material under testing placed on a silver filter, respectively. =1 is used as a reference for silver filters.  b Filter Transparency Index , where and are the XRD intensities measured in the range of silver primary peak profile (Cu anode) on a blank silver filter, and on a blank filter of the material under testing placed on a silver filter, respectively. =1 is used as a reference for silver filters.  c Interference is due to the silver filter placed under the filter of the material under testing.  d The analyst should be aware that for any filter pore size the recovery might not be complete. | | | | | | | | | |

### Other equipment

Fume cupboard, to contain dusts, vapours and gases.

Beakers, latex gloves, tongs, and powder spatulas.

Ultrasonic bath sonicator - for breaking up the agglomerated particles of samples contained in beakers.

Magnetic stirrer, with thermally insulated top, to ensure homogeneous distribution of particles in the 2-propanol suspensions contained in volumetric flasks.

Volumetric pipettes, for the desired aliquots.

Volumetric flasks, with polyethylene stoppers for the preparation of 2-propanol suspensions of calibration powders.

Pump, to generate vacuum and rapidly filter the suspension.

Vacuum filtration assembly - A typical assembly with a side arm vacuum flask, with a 25-mm filter holder is shown in Figure 1. When in use, the flask is clamped to a ring stand to prevent it from falling over, and connected to the pump with vacuum tubing.

15

10

5

VOL.

mL

125 mL

1

2

3

4

5

6

7

10

Dimensions in centimetres

**Key**

|  |  |  |  |
| --- | --- | --- | --- |
| 1 | glass funnel |  |  |
| 2 | spring clamp |  |  |
| 3 | 25 mm filter |  |  |
| 4 | vacuum base with sintered disc |  |  |
| 5 | rubber stopper |  |  |
| 6 | receiver flask |  |  |
| 7 | to pump |  |  |

**Figure 1 — Example of a filtration apparatus suitable for powder deposition on filters**

## Equipment for sample treatment and reagents

### Furnace

A furnace capable of operating up to 1000 °C may be required to remove interfering substances (see Annex C). The material is placed into platinum or glazed ceramic crucibles with lids.

### Reagents

Deionised water. 2-Propanol. 2 M HCl: 16.4% v/v (carbonate dissolution). Glacial acetic acid, 10% solution (v/v) (carbonate dissolution).

# Sampling

The sample from bulk material submitted for analysis should be as far as possible representative of the whole material. Sampling of particulate materials shall be performed according to ISO 14488. Depending on its size and physical state, this sample shall be stored in an appropriate sample bag or container, and an identification label will be attached allowing proper tracking to the source.

The minimum quantity of bulk material to be collected should be defined before the sampling is performed. Contact the analytical laboratory to determine the quantity needed, based on discussion of the method chosen for the analysis (see Note in 5.4.3) and the purpose of the results.

As much information on the sample as possible should be provided to the analytical laboratory.

Note: For example, it may be indicated how the sample was collected, what silica polymorphs and possible interference it may contain, how the sample was formed, including temperature and pressure if applicable. This information may be based on previous analyses or a knowledge of the sample and process involved. If the sample contains natural, unreacted raw materials or if the sample has been processed (chemically, thermally or otherwise), this information is important to suggest the phases that might be present (see Annex B).

If the results have legal implications, standard procedures for collecting and processing the samples can be required, and the desired minimum level (fraction percentage) for quartz and/or cristobalite quantitative determination should be specified to the laboratory.

# Specimen preparation

## Generalities

The preparation of the specimen is one of the more critical steps in quantitative XRPD analysis, and the success of the analysis will largely depend on the correct preparation for the specimen being analysed. In the analytical laboratory, the bulk sample is reduced to a loose powder and a specimen is prepared for analysis. Care must be taken to ensure that the physical state and composition of the prepared specimen be as close as possible to that of the original sample. Steps taken to homogenize and sub-sample the sample further for analysis should follow procedures in ISO 14488 and should be documented.

Although it is desirable to obtain the required information with the least amount of sample treatment, the specimen preparation may involve a number of steps such as:

- crushing a block of material;

- grinding the crushed material;

- treating the powder to remove interferences;

- drying the powder if it is wet;

- depositing the powder on a filter (thin layer specimen) or mounting it in a specimen holder (specimen of infinite thickness).

Two types of specimen preparations are included in this document:

- specimen of “infinite” thickness, mounted in a specimen holder;

- “thin” layer specimen, deposited on a filter.

A specimen is said to have infinite thickness when its thickness is greater than the beam penetration depth, i.e. according to EN 13925-2, when the diffracted intensity is at least 99,9% of the maximum attainable by increasing the specimen thickness. This infinite thickness, can be calculated (expressed in centimetres) as:

where

|  |  |  |
| --- | --- | --- |
|  |  | is the specimen density (g cm-3); |
|  |  | is the weighted sum of the mass attenuation coefficients (or mass absorption coefficients, cm2 g-1) of the constituent elements of the material; |
|  |  | is the X-ray diffraction angle (°). |

The formula is valid for a “solid” specimen, and the effective thickness can be obtained by dividing by the granular volume of the specimen (generally >70%, porosity <30%) when minimized by good specimen packing. In practice, the specimen thickness equals the thickness of the specimen holder (see 5.1.2) in which it is mounted, that is always much greater than the beam penetration depth.

Note: Hence, the effective infinite thickness of a specimen is dependent on porosity and the mass attenuation coefficients of the phases, since absorption affects the beam penetration depth. Figure 2 left, shows the range of possible penetration depths of CuKα at diffraction angles from 20° to 60° 2θ in a wide range of μ' values, for specimens with 30% porosity. For a specimen made of a pure quartz powder (ρ'=2,65 g cm-3, μ'=34 cm2 g-1), an effective infinite thickness t=0,01261 cm is calculated for the diffraction primary peak (θ=13,33°) if a Cu anode is used.

The deposition of a powder on a filter to produce a “thin” layer specimen, and its analysis by XRPD according to an external standard method, is a procedure derived from the analysis of airborne dusts collected on membrane filters (e.g. ISO 16258-2 [2]). This methodology involves the construction of a calibration curve by measuring the intensity of a diffraction peak from specimens of pure quartz/cristobalite with known masses deposited on filters. The analytical approach assumes that the diffracted intensity is a linear function of the irradiated specimen mass, after a correction for the X-ray absorption (due to the powder load thickness). This correction is calculated by measuring the transmittance of the specimen (see Annex D.1.1.3), and is more accurate when a small increase in powder load produces a great decrease of transmittance, i.e. when the powder load is low. This document considers acceptable a load on the filter that produces a change in the slope of the curve transmittance vs. load (mg) lower than 15%. The field of acceptable loads for specimens within a wide range of mass attenuation coefficients is shown in Figure 2 right, for deposition diameters of 1,5 and 2,0 cm.

Note: According to AFNOR [3] the maximum load of powder on a 25-mm filter achievable without any losses from the filter due to its manipulation should not exceed 10 mg, but this is greater than the recommended maximum mass for quantification (see Figure 2 right).

**Key**

|  |  |
| --- | --- |
| °2θ | diffraction angle |
| etinfinite | effective “infinite” thickness (μm) |
| T | transmittance |
| LOAD | Powder load on the filter (mg) |

**Figure 2 — Left: Effective infinite thickness (porosity included) calculated for a 5% quartz – 95% albite mixture (μ'=33 cm2 g-1) and a 5% quartz – 95% hematite (μ'=177 cm2 g-1), for 2θ angles from 20° to 60°. Right: Thin specimens, variation of transmittance calculated for the same mixtures, when the diameter d of the deposition area on the filter is 1,5 cm or 2,0 cm**

## Crushing

If the sample is a block (e.g. a rock, brick, slab, or product fragment) or a very coarse material, it has first to be comminuted to a more manageable sizes. This is achieved by reducing the sample into smaller pieces, for example using a masonry hammer or jaw crusher (see 5.4.2). The amount of material, and the fragment size obtained, depends on the process and machine employed to reduce the material to the desired particle size. A fragment with a length of about 4 mm or less is an ideal size for several types of grinding mills that are used to prepare powders with µm sized particle diameters for XRPD quantification.

## Grinding

XRPD analysis requires the grain size of the specimen to be very fine, because differences in particle sizes can modify the diffraction peak intensity and breadth, affecting quantification. Rarely, the grain size of a bulk sample falls already in the right range for XRPD. In this case, the sample does not require any grinding and a specimen can be prepared by directly mounting the powder in the specimen holder. In all the other cases, the grain size distribution of the sample will not be in the optimum range for XRPD analysis, and the material grain size should be reduced by grinding, even if the material is already a powder or a mud.

Note 1: Particle inhomogeneity and particle statistics - In Bragg-Brentano geometry, the intensity of diffraction peaks depends only on crystallites having the relevant lattice planes almost parallel to the specimen surface. Because the X-ray penetration into a specimen is small, problems can occur when the individual particles are large relative to the penetration depth of the X-ray beam. In this case, the number of crystallites could be too small, and errors in the intensity measurements could be introduced.

Contamination by the grinding elements should not significantly affect the analytical result for CS, but excessive grinding can produce amorphization of quartz and cristobalite crystals, reducing their diffraction intensities.

Note 2: For samples with extremely low content of CS, contamination from grinding equipment might represent a significant issue. Dedicated grinding equipment might be needed in this case.

The particle size distribution of the CS crystallites in the unknown specimen after grinding should ideally match that of the reference material or internal standard used for the analysis (see 5.3.1 and 5.3.2). Intensities of the same peak measured in different specimens can only be compared if the number of crystallites contributing is proportionally the same. In order to achieve particles in the optimal size range distribution, a laboratory mill is generally needed (see section 5.4.3).

Note 3: The powder produced directly by manually grinding using mortar and pestle is often too coarse, and this grinding method is not suggested in this document.

The appropriate grinding time and settings to achieve the required particle grain size should be defined by a test and trial procedure, checking the grain size distribution by using, for example, one of the techniques described in Note 4, until it falls within the optimum range. However, when samples agglomerate or “cake” during grinding, further particle size reduction is suppressed.

Note 4: A number of methods (ISO 13317 - gravitational liquid sedimentation methods: fixed pipette method [4], and X-ray gravitational technique [5]; ISO 13319 - electrical sensing zone method [6]; ISO 13320 - laser diffraction methods [7]) and instruments (particle sizers) are available for the determination of particle size distribution, typically in the size range from 0,1 μm to more than 100 μm.

Note 5: In an alternative preparation approach (calibration graph analytical method described in 8.4.5), weighed proportions of pre-ground sample and internal standard materials are mixed, and then subjected to a final grinding/mixing step in a laboratory mill. In this case, the grain sizes of sample and internal standard powders before the final grinding should be slightly greater than the XRPD optimum grain size, so that the desired size is achieved at the end of final grinding. If a ductile mineral is used as internal standard (e.g. nickel oxide, NiO - bunsenite), a fixed amount (e.g. 1/5 of the specimen weight) of a very hard material, whose XRPD signals do not overlap with CS and nickel oxide reflections, can be added to the sample-internal standard mixture before the final grinding, to act as a buffer evening out the grinding, i.e. so that particles of different mineral phases will be ground to the same extent, independently of sample composition [8]. Gamma aluminium oxide Al2O3 nano powder, that shows an amorphous structure with a small crystallization degree, is suggested as a grinding agent.

Two main grinding approaches are available: dry grinding and slurry grinding.

- Dry grinding is sometimes simpler and quicker, but requires careful matching of the technique to the sample. If caking is due to moisture, as in many soils or cements, the sample should be dried before grinding.

Note 5: Lubricants (dry soap or detergent), antistatic agents, abrasives, or binding agents can be used as grinding aids. For example, propylene glycol (one drop for up to ten grams of sample) can be used for laboratory fine grinding of Portland cement and some minerals. In case they contribute to the sample, these additives cannot be used with some methods unless they are included in the calibration process.

- In slurry grinding, particles are suspended in solution during grinding. Water, alcohol, or another liquid is added to the sample before grinding, and has to be removed afterwards. Slurry grinding is a reliable way of grinding a sample to micron-sized particles, but it can be time-consuming. Clay samples generally can be analysed without any grinding.

The ground material can be mixed, without further grinding, using a mortar and pestle (see 5.4.4), split into equal parts (quartering), and finally one of the parts used for mounting in the specimen holder, or deposited onto an analysis filter.

If using calibration standards that are consistent with the respirable aerosol fraction convention (aerodynamic diameter cut point of 4,0 μm), the sample grain size should be in a comparable range, i.e. should have a mean particle size of approximately 2,5-3,0 μm diameter (for material density around 2,6).

Note 6: For special purposes, the selection and collection of the desired grain size fraction for calibration standards and samples can be achieved by sedimentation: the sample is dispersed in water or another suitable liquid, and after a calculated sedimentation time the supernatant of the dispersed sample is collected and dried (EN 17289-3 [9]).

## Drying

If slurry grinding has been carried out with water, the wet slurry should be poured in a wide Petri dish, and placed in a laboratory oven at 90 °C until dry (at a lower temperature and in a fume hood if organic liquids are used). Clay samples should be dried in an oven at about 40°C. The wet ground material should be allowed to evaporate before analysis or further processing. The lumps in the dried mixture are then broken up with a pestle and mortar.

## Pre-concentration and removal of interfering phases

To improve the detection limit of the analysis, some treatments can be applied, such as pre-concentration to eliminate the non-silica phases in a sample. In fact, quartz and cristobalite are sufficiently inert for many phases to be removed in their presence by chemical methods. Strategies to remove mineral phases without affecting the crystalline silica phases in the sample are presented in Annex C.

If some non-silica phases have been removed from the sample, the weight fraction of the CS phase in the treated sample , determined by XRPD (see 8.4.4.3, 8.4.5.3, and 8.4.6.2), must be corrected by multiplying it by a concentration factor *CF*, given by:

where

|  |  |  |
| --- | --- | --- |
|  |  | is the mass of the dry bulk sample weighed after the treatment; |
|  |  | is the mass of the dry bulk sample weighed before the treatment. |

Note: Example - A sample made of a solid block is crushed and milled obtaining a fine powder, then dried in an oven. A sub-sample is selected, placed in a weighing bottle and weighed. Its weight results =10,00012 g. This sub-sample is then treated to eliminate a non-silica phase. After the treatment, the sub-sample is dried in an oven, placed in a weighing bottle and weighed. Its weight results = 7,75009 g. The concentration factor is calculated as 7,75009 / 10,00012 = 0,7750. A quantitative XRPD analysis for quartz is carried out on a specimen prepared by using the treated sub-sample powder, giving = 1,3%. The weight fraction of quartz in the original sample is 1,3% ∙ 0,7750 = 1,0%.

## Weighing and mounting of a specimen of infinite thickness

The back packing in a specimen holder is a standard technique mostly used to fill the cavity of the powder mount for analysis of CS phases, but other types of specimen holders may also be used (see 5.1.2). Although this preparation technique subjects the particles to some crystallographic preferred orientation, experimental evidence shows good measure repeatability when quartz and cristobalite are the analytes.

Preparation of a specimen for the “internal standard method” and the “spiking method” requires the addition of known weight fractions of a reference material to the specimen. The following procedure is suggested.

1. Estimate the weight mass that the specimen should have, and calculate the masses of reference material , and sample , necessary to obtain the weight fractions and required by the analytical method.

Note: A few weighing tests can be carried out in the laboratory to determine the weight mass that generally fills the specimen holder used for analysis. For example, if the average weight results 1,95 g, a mass = 2 g in slight excess of that necessary to fill the specimen holder can be considered.

1. Weigh two clean and dry glass weighing bottles with lids, avoiding direct contact of the glass with the fingers.
2. Add an amount of sample in the first weighing bottle and obtain, by trial and error, a mass of sample around the optimum value ±1%, (mg).
3. Add an amount of reference material in the second weighing bottle; the required mass of reference material will be obtained by trial and error, with a tolerance range of ±1%, (mg).
4. Calculate the effective percentage weight ratio: .
5. Pour the weighed sample and reference material in a mortar, and gently mix the resulting powder until the mixture is uniform.

When the powder mixture has been prepared, mount it in a specimen holder by using the specific preparation kit. For back filling, proceed as follows (Figure 3).

1. Clamp the specimen holder ring to the preparation table and spread the powder in the holder ring.
2. Press the powder down firmly in the holder ring using the powder press block.
3. Scrape any powder that flows out using a spatula, and press down again.
4. Repeat the operations until no surplus powder remains and the surface is flat and uniform. Only a very small amount of the powder mixture should remain in the mortar, unused.
5. Place the bottom plate onto the holder ring.
6. Remove bottom plate and holder ring from the preparation table, and the specimen is ready for XRPD analysis.

## Weighing and deposition of thin layer specimen on filter

“Thin” layer specimens in this document are obtained by depositing 1-5 mg of powder representative of the sample on a porous, 25-mm diameter filter. Silver, PVC, mixed esters of cellulose, and polycarbonate filters can be used for deposition and analysis (see 5.5.1).

A representative fraction of the powdered sample, included in the weight range 1-5 mg, is placed into a beaker, covered with a few millilitres of 2-propanol, and placed in an ultrasonic bath for about 5 minutes. The material is then poured into a filtration apparatus (see 5.5.2) and collected on to a membrane filter for the analysis. The weight of the specimen, , is determined by weighing the filter before and after the deposition.

A procedure for the preparation of calibration filters is detailed in Annex D.1.1.1.

Note: Quartz particles deposited on membrane filters exhibit a slight preferred orientation enhancing the (101) diffraction line, but not to the extent of specimens prepared by powder loaded by back-packing in a specimen holder.

A

13

8



4

1

2

5

3

7



10

12

11

9



6

B

C

D

E

F

**Key**

|  |  |  |  |
| --- | --- | --- | --- |
| 1 | preparation table |  |  |
| 2 | press block |  |  |
| 3 | holder ring |  |  |
| 4 | bottom plate |  |  |
| 5 | spatula |  |  |
| 6 | mortar and pestle |  |  |
| 7 | grinded powder |  |  |
| 8 | heap of powder |  |  |
| 9 | press the powder |  |  |
| 10 | scrape out the powder in excess |  |  |
| 11 | the surface is flat and uniform |  |  |
| 12 | place the bottom plate onto the holder ring |  |  |
| 13 | the specimen is ready |  |  |

**Figure 3 — Example of specimen preparation according to the back filling technique**

# Analysis

## Symbols

In this document, a mineral phase is indicated by *i*, and its associated generic peak by *j*. The primary, secondary, and tertiary peaks of a phase are shown as *j*=1, *j*=2, and *j*=3.

The symbols *Qz* and *Cr* are used for parameters that refer to the polymorphs quartz and cristobalite respectively, while the symbol *CS* is used when the two polymorphs of crystalline silica can be considered in the same way. Hence, the symbols *Qz1* and *Cr1* refer to the primary peaks of quartz and cristobalite, and *CS1* refers to the primary peak of a generic crystalline silica phase.

The symbol *Met* is used for the peak originating from the metal phase of the filter, or the disc, required for the absorption correction (see Annex D.1.1.3), or the symbol *Ag* for silver, *Al* for aluminium, *Zn* for zinc, when the metal phase is specified.

The symbol *ref* is added to the mineral phase symbol when the analysis refers to its reference material. The symbol *rel* means relative, and is used for relative intensity.

## Parameters of a diffraction line profile

The parameters of a diffraction line, measured in the 2θ region of the diffraction effect (range of line profile), used for both qualitative and quantitative analyses in this document are (Figure 4):

- line position: 2θ location of the maximum of the diffraction line;

- intensity, (net area in counts·°2θ) of a peak j: area of the diffraction line above the background;

- line width: the Full Width at Half Maximum (FWHM), i.e. the line breadth at half of the peak height;

- asymmetry *As*=*LHS*/*RHS*, is defined by breadth parameter on each side of the maximum of the diffraction line found by the software, where *LHS* is the distance from the centre line to the left hand side and *RHS* the distance from the centre line to the right hand side of the peak.

Note 1: The background signal of a peak can generally be fitted using a straight line (as in Figure 4). When the analysis includes a wide range of line profile, a dedicated software can also be used to fit the background signal with a different appropriate mathematical function.

The diffraction intensity of a peak can be calculated using either directly the raw data (as in Figure 4) or the data after fitting the profile shape using a computer program based on least-squares or maximum likelihood methods. While pattern decomposition to unravel overlapping diffraction line profiles is not in the scope of this document, the analyst can apply professional judgement in using deconvolution techniques in case of complex interferences.

**Key**

|  |  |
| --- | --- |
| I | intensity (counts) |
| °2θ | diffraction angle |

**Figure 4 — Characteristics of a diffraction line, in this example the third most intense peak of cristobalite (102), Cr3. In this example, the software calculates the peak position by fitting a parabola (solid line) to the data points close to the maximum intensity. The net height is the maximum of the parabola used to find the position of the peak, measured from the background line to the top of the peak.**

## Instrument conditions

The analyst should choose an optimized set of the variable instrument parameters:

- X ray tube material and type;

- power settings, with higher values giving better sensitivity;

- constant beam divergence vs. constant irradiated length;

- slits and mask;

- spinner;

- detector and monochromator;

- acquisition program: step size, time per step, 2θ scan range. A minimum of 5 data points above the half maximum are needed for each diffraction line used for phase quantification.

## Analytical methods

### Choice of the analytical method

This document proposes three analytical methods that can be applied to bulk samples ground to a fine powder. The resulting percent weight fraction of CS obtained for a sample should be the same, within the analytical uncertainty, independently on the used method. Each method presents some advantages and limitations, and its use can be more appropriate in specific cases.

- The external standard method, where the sample is deposited as a thin layer specimen onto a filter is especially useful when the available sample weight is very low (down to few milligrams of powder), so that a specimen of infinite thickness, cannot be prepared. It is recommended that the powder collected on the filter should have an average grain size below 5 μm and possibly in the range of the respirable grain size (D50≈2,5 μm for CS powder), because the filter is generally not able to efficiently retain coarser grain size, and losses of particulate are expected during the handling of the filter. It has also to be underlined that the measurement uncertainty is expected to be greater than those achieved by the other methods presented in this document.

- The internal standard method applies to a specimen of infinite thickness and is the most frequently used of any of the methods for quantitative phase analysis by XRPD. The method can be used if the amount of the dry sample is at least a few grams, so that it can be ground in a laboratory mill and a specimen of infinite thickness can be prepared. Two variants of the method are included in this document, both with similar advantages and limitations. Although the method could be used over the entire range of possible CS concentrations, better sensitivity could be produced by the spiking method when the CS weight fraction is very low.

- The spiking method also applies to specimens of infinite thickness, so it can be used if the amount of the dry sample weight is at least a few grams. The mass absorption coefficient of the sample is generally not known and is not taken into account by this method; hence, the method is used on the assumption that the additions of a dopant to the sample determine negligible changes in its mass absorption coefficient. In practice, this assumption is generally valid if the added CS percent weight fraction is relatively small, for example below 20, or when the mass absorption coefficient of the sample is known to be close to that of quartz and cristobalite. The calibration line used for the analyte quantification works effectively if the amounts of dopant are in the same range of the CS amount in the sample, which can be approximatively estimated by a preliminary XRPD analysis on a specimen without any dopant addition.

Note: The mass absorption coefficients of quartz and cristobalite are known to be approximately μ'=34 cm2 g-1. Samples with mass absorption coefficients in the range between 27 and 40 cm2 g-1 introduce a small error in the determination, and allow the use of the spiking method over the entire range of possible CS concentration.

### Calibration specimens, reference diffraction patterns and reference values

Reference values and reference diffraction patterns of quartz and cristobalite should be obtained in the laboratory by analysing the same specimens used for calibration. They are used for both phase identification and quantification. The preparation characteristics of the calibration specimens depend on the specific method chosen for quantitative analysis.

- External standard method on thin layer specimen - The calibration specimens (or “calibration filters”) are prepared with pure CS reference materials deposited on filters, and used for the construction of calibration lines (see 8.4.4.2).

- Internal standard method on specimen of infinite thickness - The calibration specimens are prepared by mixing fixed proportions of pure CS reference material and internal standard material, and used for the determination of RIR value or the construction of calibration lines (see 8.4.5.2).

- Spiking method on specimen of infinite thickness - A reference specimen is prepared with pure CS reference material, and used for the estimate of the weight of CS reference material to be added to the sample (see 8.4.6.2).

The calibration specimens should be prepared and analysed in the laboratory by following the same preparation procedure, and analysis setup, later used on unknown specimens. Therefore, the reference diffraction patterns will present effects such as preferred orientation, extinction, microabsorption, and surface roughness similar to those found in the unknown specimen, and these effects will be, at least in part, compensated for in both qualitative and quantitative analyses.

Details for calibration specimen preparation, analysis, and calculation are given in the sections that follow and in Annex D.

For each of the three most intense lines *j* of the CS phase, the following parameters (see 8.2) are determined and taken as references, indicating them by adding the index *ref*:

- reference location of the maximum of the diffraction line, (expected values are reported in Annex A);

- reference intensity, (net area in counts·°2θ);

- reference Full Width at Half Maximum, (°2θ);

- reference asymmetry, .

The reference relative intensity of the strongest peak is set by definition as =100. The reference relative intensities of secondary and tertiary peaks *j* are then calculated as.

Note: For example, if the reference intensities for quartz are =8913 counts·°2θ, and =1454 counts·°2θ, then the reference relative intensity of Qz2 is (1454 / 8913)·100 = 16,3. The ratio between the reference relative intensities of Qz3 to Qz2 is also calculated and recorded. Expected values of reference relative intensities are reported in Annex A.

### Quartz and cristobalite identification: preliminary qualitative analysis

For all the analytical methods in this document, a XRPD scan is carried out on a specimen of sample unmixed with any internal standard, for CS identification.

The line positions for the three most intense peaks of the CS phase found in the experimental diffraction pattern are compared with those measured for pure quartz and cristobalite in their reference patterns (see 8.4.2). A peak angular shift can be generated due to a slight specimen height displacement, resulting in defocusing. The consistency of the peak shift along all the diffraction pattern angular range should be evaluated, and the offset consequently corrected.

Note 1: If the concentration of CS in a specimen is very low, not all the peaks reported in the reference patterns are observed in the experimental diffraction pattern, especially when the specimen is deposited as a thin layer on a filter.

Note 2: The analysis can be improved by carrying out a continuous scanning over a wide range including the three most intense CS lines, for example between 19 °2θ and 52 °2θ if a copper anode is used, and then considering all the CS peaks observed in the analysed range.

If a positive match between the line positions in unknown specimen and reference patterns is found, the diffraction patterns are visually examined, looking for double peaks, shoulders, and other anomalies. Then, the diffraction intensities , , of the peaks identified as quartz or cristobalite in the unknown specimen are measured, and the relative intensities calculated:

The relative intensities, , are compared with the reference relative intensities, (see 8.4.2). An imbalance of relative intensity within ±15% between experimental and reference values can generally be considered a positive match for the two most intense peaks of quartz and cristobalite. Where the imbalance lay outside this range, the analyst should consider all the measured parameters and, based on his/her experience, eventually might consider the presence of interferences. Greater differences are often found in case of less intense peaks. Annex B reports the potential mineral interferences.

### Quantitative analysis by the external standard method

#### Generalities

This XRPD method determines the weight of CS in a thin specimen deposited on a filter, while the total weight of the specimen is determined by weighing the filter before and after the deposition of the powder, therefore the CS weight fraction can be readily calculated. The weight of CS in the specimen is determined from the X-ray response calibrated against filters loaded with known amounts of the pure CS reference material. The calibration filters are prepared from aliquots of a suspension of CS reference material. The analytical approach assumes that diffraction intensity is a linear function of the irradiated CS weight. However, the measured intensity deviates from the theoretically linear intensity because the X-ray radiation is partially absorbed by the specimen’s matrix, and a correction factor has to be used.

This method can be used over the entire range of CS possible concentration in a sample.

#### Calibration curves

The calibration filters should be prepared by using the same filtration apparatus, and analysed by the same instrument, instrumental setting, and acquisition programs that will be used for unknown specimens. A detailed procedure for the preparation of calibration filters is presented in Annex D.1.1.1.

A correction factor for absorption is calculated by measuring the attenuation of diffraction intensity of a peak from the material underlying the specimen, not overlapped with any peak of the specimen (calculation procedure in Annex D.1.1.3). A metal is a good choice, represented by the same filter used for specimen deposition, if it is a silver filter, or by the metallic phase forming the support plate placed under the filter, if an organic filter transparent to X-ray radiation is used for specimen deposition.

The primary peak of the metal phase (*Met1*) from the filter or the support base is then analysed before and after calibration specimen deposition. When an organic filter is used, the analysis should be run by placing the deposition filter on the same support plate.

Note 1: The positions of the primary peaks of metal phases are found in a section of the diffraction pattern where no quartz or cristobalite major reflection is located (silver: Ag1=38,12 °2θ; aluminium: Al1=38,47 °2θ; zinc: Zn1 = 43,22 °2θ, for Cu radiation), so they generally are fully resolved.

Note 2: An automatic divergence slit may preferably be used, so that the same filter area is analysed for all the CS and metal peaks, and transparency to X-ray radiation can be best determined.

Before the calibration specimens are deposited on the analysis filters, the filters are weighed. The weight of CS reference material to be deposited on filters should range from a very low value (e.g. *Wmin*=0,01 mg) up to the maximum weight allowed for the preparation of the unknown specimens (e.g. *Wmax*=5 mg). At least 10 calibration filters will be prepared with variable weights between *Wmin* and *Wmax*. An example for a preparation plan is given in Annex D.1.1.1.

The calibration filters are mounted on the diffractometer and analysed. The three most intense lines of the CS phase, plus a diffraction line *Met1* from the silver filter or metal support plate, are measured on each calibration filter. The diffraction intensity of a reflection from the drift correction disc material, , is also measured.

The diffraction parameters described in section 8.4.2 are determined for each CS line. Intensities are then corrected for X-ray absorption following the procedure given in Annex D.1.1.3, obtaining the values for the each calibration filter.

For each CS reflection, the relationship between corrected intensities and CS weights are used to derive a calibration function. Generally, a straight trend line is calculated according to the method of least squares, where the overall solution minimizes the sum of the squares of the residuals made in the results of every single equation. The linear regression analysis is based on the equation:

where

|  |  |  |
| --- | --- | --- |
|  |  | is the weight of the CS phase; |
|  |  | is the intercept with the y-axis; |
|  |  | is the slope of the line. |

An example of calibration lines construction is given in Annex D.1.1.4.

Note 1: A trend line can be forced through zero, or also a regression weighed for the precision of counting may be used. Given the heavy loadings on the filters considered in this method (up to 5 mg), the wide range of possible CS weight that has to be represented can be calibrated by using two or three regressions for different parts of the range (for example: 0-0,1; 0,1-1 and 1-5 mg) with different slopes and intercepts.

Note 2: A non-linear function may also be used.

#### Analysis of an unknown sample

The specimen is prepared according to the procedure given in Annex D.1.1.1, and analysed by using the same instrument, instrumental setting, and acquisition programs used for calibration filters. The weight of the specimen on the filter, , is calculated by weighing the filter before and after powder deposition.

The XRD analysis is run on the specimen to determine the values , , , and for the three most intense reflections of the CS phase, the values and of the primary reflection of the metal underlying the specimen. The reference peak of the drift correction disc material is also analysed, for example at the beginning and ending of each working session, and its average diffraction intensity, , is calculated.

After the analyses, the line positions are corrected for displacement (procedure in Annex D.1.2.4), and the diffraction patterns are studied for CS phases identification (see 8.4.3).

If a CS phase is identified, its diffraction intensities are corrected for absorption and for the drift in XRD radiation intensity over time, :

where

|  |  |  |
| --- | --- | --- |
|  |  | is the correction factor for absorption (see the calculation procedure in Annex D.1.1.3); |
|  |  | is the correction factor for the drift in X-ray radiation intensity since the day of instrument calibration (see Annex D.1.2.5). |

If no interference is observed on the CS primary peak, its diffraction intensity is used for quantitative analysis. If an interference is present on the primary peak of CS, the secondary peak diffraction intensity can be used if free from interference, but it will result in decreased sensitivity.

The weight of the CS phase, , is:

where

|  |  |  |
| --- | --- | --- |
|  |  | is the intercept of the appropriate calibration curve; |
|  |  | is the slope of the appropriate calibration curve. |

Finally, the percent weight fraction of the CS phase, , in the specimen is calculated:

The same analytical procedure is performed on a second specimen from the same sample.

The percent weight fraction of the CS phase in the sample is then calculated as the average between the results from the two specimens. If the relative difference between the two results is greater than 10% the reasons for the difference in performance should be investigated, and in case, a third specimen can be prepared and analysed.

See Annex D.1 for an example.

### Quantitative analysis by the internal standard method

#### Generalities

Specimens of infinite thickness are prepared from a mixture with fixed weight fractions of the sample (s) and an internal standard (IS) of a mineral phase that is not present in the sample. XRPD analyses are carried out to determine the intensities of both CS and IS phases, and then their ratios are calculated.

The percent weight fraction of the CS phase in the sample is determined by comparing the intensity ratio measured in a specimen from the sample, with the reference intensity ratios determined in the same laboratory on specimens prepared from mixtures of CS and IS phases in known proportions.

In this method is not necessary to take into account the absorption factor, which is eliminated from the solving equation. In fact, the variation of absorption due to the variation of the relative amounts of the other phases present in the mixture does not affect the ratio between the diffraction intensities of CS and IS, since such variations equivalently affects both the intensities.

Two variants of the method are described in this document:

* Reference Intensity Ratio (RIR) approach – For each CS reflection *j*, a is calculated from a number of calibration specimens prepared from a mixture with a fixed proportion of CS to IS (see Annex D.2.1.2). The intensity ratio found for the specimen is directly compared with the value, and the percent weight fraction of the CS phase in the sample is determined.
* Calibration graph approach – For each CS reflection *j*, a calibration line for the variation of the ratio over the entire range of possible CS percent weight fraction is constructed by analysing a number of calibration specimens. The CS percent weight fraction in the sample is calculated by substituting the ratio found in the specimen from the sample in the equation of the calibration line. In this approach, the addition of a diluent mineral phase to the mixture is recommended (see Annex D.2.2.1).

This method could be used over the entire range of possible concentrations in a sample, but the spiking method is preferred for low weight fraction.

#### Calibration specimens

The determination of RIR values, or the construction of calibration graphs, requires the use of a number of calibration specimens, prepared by mixing CS and IS reference materials according to the procedure given in section 7.6. Analysis are performed with the same instrument, instrumental setting, and acquisition program that will be used for unknown specimens. Therefore, RIRs and calibration graphs are specific for the laboratory.

The composition of the calibration specimens is as follows.

* Reference Intensity Ratio (RIR) approach – A fixed reference percent weight fraction of internal standard, , is chosen in the laboratory, and used for the preparation of mixtures with the CS phase reference material. All the calibration specimens have a percent weight fraction as close as possible to . As a consequence, the percent weight fraction of CS reference material, , is also fixed and equal to (an example is given in Annex D.2.1).
* Calibration graph approach – The calibration specimens are prepared with a fixed reference percent weight fraction of internal standard, , variable CS percent weight fractions that increase up to , and variable percent weight fractions of a diluent, , equal to (an example is given in Annex D.2.2).

Note: A value =50 is often used for both variants, but values in the range 10-50 may generally be considered.

The calibration specimens are mounted in the diffractometer and the three most intense lines of the CS phase, plus a diffraction line *k* of the IS phase, are analysed. The diffraction line *k* of IS is conveniently chosen so that it is fully resolved and not overlapping any line from the CS phases. The diffraction parameters described in section 8.4.2 are determined for each line.

##### *Calibration parameters for the RIR approach*

The intensity ratio *IR* for each CS phase line *j* is given by:

where

|  |  |  |
| --- | --- | --- |
|  |  | is the diffraction intensity of a line *k* of the internal standard IS; |
|  |  | is the diffraction intensity of a line *j* of the CS phase; |
|  |  | is the percent weight fraction of the internal standard IS. |

The reference *IR* for a CS line, denominated , is calculated as the average from all the values.

Annex D.2.1.1 shows a scheme for calibration specimen preparation and RIR calculation.

##### *Calibration graph approach*

A number (at least 6) of calibration specimens are prepared (see Annex D.2.2.1). Each calibration specimen is characterized by its percent weight ratio between quartz and internal standard, :

in which generally varies between 1 and 100.

Each specimen is analysed for the three most intense CS phase lines *j*, and a line *k* of the internal standard IS. Then their diffraction intensity ratios are calculated:

The intensity ratio values, , are plotted along the y-axis and the percent weight ratios of quartz or cristobalite to the internal standard mass, , along the x-axis of the calibration graph. A straight calibration line is derived, for each of the three major reflections of the CS phase, according to the method of least squares:

where

|  |  |  |
| --- | --- | --- |
|  |  | is the slope of the calibration line. No intercept appears in the equation because the trend line is forced through zero. |

An example of calibration line construction is given in Annex D.2.2.1.

#### Analysis of an unknown sample

A preliminary XRPD analysis on a pure sample specimen is performed, then the diffraction patterns are inspected for CS phase identification and interferences (see 8.4.3), and the diffraction intensities , , are measured. The most intense diffraction line *j* of CS without interferences is chosen for quantitative determination. The specimen is also scanned in the range of the reference line *k* of the internal standard IS, to verify if any interference could affect the measurement of in the unknown sample.

A specimen from a mixture of sample and the internal standard, with an effective percent weight fraction as close as possible to , is prepared following the same procedure described for the calibration specimens, but with the sample *s* in place of the CS reference material. The specimen is mounted on the diffractometer, and the most intense diffraction line *j* of CS without interferences, and the reference line *k* of the internal standard IS, are analysed for the quantitative determination.

Note: If the calibration graph approach is chosen, a diluent mineral phase may also be added to the specimen in a known amount (see Annex D.2.2.2).

##### *RIR approach*

The CS phase percent weight fraction in the sample, , is calculated as:

See Annex D.2.1.2 for an example.

##### *Calibration graph approach*

The percent weight fraction of the CS phase in the sample is calculated as:

See Annex D.2.2.2 for an example.

### Quantitative analysis by the spiking method

#### Generalities

A specimen of the pure sample, and at least one more specimen with a chosen addition of the same CS mineral phase that has to be determined, are XRPD analysed. A CS reference material is used as dopant. The percent weight fraction of the CS phase in the sample is determined through a calibration line constructed for each individual sample by plotting the diffraction intensity results for the CS phase vs. the CS percent weight fractions added to the sample.

The method is used on the assumption that the additions of a dopant to the sample determine negligible changes in its mass absorption coefficient. In practice, this assumption is generally valid if the addition of CS percent weight fractions are relatively small, for example <20, or when the mass absorption coefficient is known to be close to that of quartz and cristobalite.

In this document, it is recommended that the diffraction intensities of a CS line are measured in an undoped specimen and in at least two more specimens prepared by adding to the sample known amounts of the CS reference material.

#### Analysis of an unknown sample

A specimen of the pure sample is prepared for analysis according to the procedure given in section 7.6. The specimen is mounted on the diffractometer and the three most intense lines of the CS phase are analysed.

After the analysis, the diffraction patterns are inspected for CS phase identification and interferences (see 8.4.3), and the diffraction intensities , , and are measured. The most intense CS diffraction line *j* without interferences is chosen for quantitative determination. Its diffraction intensity is compared with the reference intensity , and an approximate value of the CS weight fraction is calculated:

This estimate does not take into account the differences in absorption characteristics between the unknown specimen and the reference specimen. The result of the calculation is used to evaluate if the spiking method can be applied for the specific sample (i.e. if <20), and to calculate the masses of CS reference material that are to be added to the unknown sample for the next stage of analysis.

If this criterion is not fulfilled, a different analytical method must be used. If this criterion is fulfilled, a second (add1) and a third (add2) specimen are prepared according to the procedure given in section 7.6, by mixing known weight fractions of sample and CS dopant. The following proportion are suggested for the additions:

* addition 1:
* addition 2:

and if a third specimen is prepared, to improve the result:

* addition 3:

The doped specimens are mounted on the diffractometer and analysed over a °2θ range that cover the chosen line *j* of the CS phase. Then, the diffraction intensities and are measured.

A graph with the three diffraction intensities (, , and ) as a function of their CS percent weight fraction additions (zero, , and ) is constructed. The diffraction intensity of the peak should result a linear function of the dopant, and the slope *a* and intercept *b* of this line are calculated.

The percent weight fraction of the CS phase in the unknown sample is:

See Annex D.3 for an example.

# Performance characteristics of the methods

## Limits of detection and quantification

The limits of detection (LOD) and quantification (LOQ) are defined as the lowest “amounts” of an analyte that are detectable and quantifiable (ISO 18158). For the determination of an analyte in a bulk sample, it is appropriate to replace the term “amount” with “weight fraction”, to define the and the of an analyte . When the determination is carried out by XRPD, the limit values also depend on the phase peak () used for the determination, therefore this information should be provided, and the appropriate symbols and should be used to represent the limits of detection and quantification.

Note 1: The limits of detection and quantification depend not only on the analytical method itself, but also on the instrument, instrument settings and acquisition program used, and therefore should be experimentally determined in each laboratory. Nevertheless, typical values can be estimated and are provided in Annex E.

The limits of detection and quantification can be determined for the phase peaks not affected by interferents. A “major” interference affecting a peak does not allow calculating a reliable XRD intensity, therefore and cannot be determined, and a different peak should be used for quantitative determination. If the three most intense peaks of quartz or cristobalite are affected by major interferences, the analytical methods described in this document should not to be used.

Note 2: The experience of the analyst is crucial to evaluate when an interference can be considered as a “major” interference, and therefore a different peak has to be used for quantification and for the determination of LOD and LOQ.

Multiphase polycrystalline samples often produce complex diffraction patterns, where a certain degree of interference is observed on the three most intense peaks of quartz or cristobalite. The limits of detection and quantification determined on quartz and cristobalite primary peaks not affected by interferents can therefore be considered as “best possible limit values”. The best possible limit values are the lowest values for peaks that are not affected by interferents.

Examples of calculation of the limits of detection and quantification are provided in Annex E.

Note 3: Limits of detection and quantification, as provided in Annex E, are determined in terms of counts heights. The analyst should record both height and area for calibration.

## Uncertainty of measurement

ISO 24095 provides guidance about how to calculate the uncertainty of respirable CS measurements to comply with ISO/IEC Guide 98-3 [10] and gives examples of the uncertainty associated with a reported value.

The performance requirements for laboratory tests do not include a maximum allowable uncertainty or inaccuracy in terms of relative error, such as those generally intended for occupational hygiene measurement methods.

Note: Although not compulsory, it is a good practice to determine the uncertainty of the measurement, that can inform on the use of the data.

The results of an inter-laboratory study implemented for the estimation of measurement uncertainty when the three XRPD methods presented in this document are used to determine the weight fraction of quartz in bulk samples are provided in Annex F.

# Test report

## Minimum report requirements

The test report shall contain at least the following information (ISO/IEC 17025):

1. the name and address of the laboratory;
2. identification of the report;
3. details of the analytical method used, with reference to this document;
4. the name and the model of the diffractometer used for the analysis;
5. the reference materials used for the calibration;
6. the LOD and LOQ;
7. the estimated expanded uncertainty;
8. the storage period of the samples;
9. the date of the analysis;
10. a complete identification of the sample;
11. the percent weight fraction of analyte (quartz and/or cristobalite);
12. all operating details not specified in this document, or regarded as optional, together with details of any incident that may have influenced the results;
13. the name of the analyst;
14. the signature of the laboratory manager or a person delegated by the laboratory manager

## Data to be archived by the laboratory

The following is the minimum that should be archived by the laboratory:

1. 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;
2. the calibration curves;
3. a copy of the test report sent to the customer;
4. a copy of the scans and parameters of the instrument;
5. the samples, for a period of time to allow analyses to be verified.
6. (informative)  
     
   Expected line positions and relative intensities of quartz and cristobalite

The values of Miller indices (*hkl*), angular positions for Cu radiation (*2θ*), interplanar spacings (*d*), and relative intensities (*I*) are given in Tables A.1 (quartz) and A.2 (cristobalite), from PDF cards by the International Centre for Diffraction Data [11]. Data are referred to the angular range between 19 to 52 °2θ (for Cu radiation). Only relative intensities greater than 1 are reported.

**Table A.1 — Quartz – Average values, for Cu radiation, from 3 PDF cards: 00-046-1045; 01-070-3755; 01-070-7344 [11]**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Symbol** | **Miller indices**  *hkl* | **Peak position** a | **Interplanar spacing** | **Relative intensity** b |
| *2θ* | *d* | *Irel* |
| ° | Å |  |
| Qz2 | 100 | 20,85 | 4,256 | 18,8 |
| Qz1 | 101 | 26,63 | 3,344 | 100,0 |
|  | 110 | 36,54 | 2,457 | 7,7 |
|  | 102 | 39,45 | 2,282 | 7,1 |
|  | 111 | 40,28 | 2,237 | 3,2 |
|  | 200 | 42,44 | 2,128 | 5,0 |
|  | 201 | 45,78 | 1,980 | 3,0 |
| Qz3 | 112 | 50,12 | 1,818 | 11,6 |
| NOTE Quality Mark: Star; Status: Primary, Pressure/Temperature: Ambient; System: Hexagonal; Space Groups: P3221 (154) and P3121 (152).  a Radiation: CuKα1 - 1.5406 Å.  b Fixed slit intensity. | | | | |

**Table A.2 — Cristobalite – Average values, for Cu radiation, from 3 PDF cards: 00-039-1425; 01-074-9378; 04-007-2134 [11]**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Symbol** | **Miller indices**  *hkl* | **Peak position** a | **Interplanar spacing** | **Relative intensity** b |
| *2θ* | *d* | *Irel* |
| ° | Å |  |
| Cr1 | 101 | 21,97 | 4,043 | 100,0 |
|  | 111 | 28,42 | 3,138 | 7,8 |
| Cr3 | 102 | 31,42 | 2,845 | 8,7 |
| Cr2 | 200 | 36,06 | 2,488 | 11,7 |
|  | 112 | 36,35 | 2,470 | 4,9 |
|  | 211 | 42,63 | 2,119 | 2,0 |
|  | 202 | 44,80 | 2,021 | 2,5 |
|  | 113 | 47,00 | 1,932 | 3,9 |
|  | 212 | 48,57 | 1,873 | 4,4 |
| NOTE Quality Mark: Star; Status: Primary, Pressure/Temperature: Ambient; Crystallographic system: Tetragonal; Space group: P41212 (92).  a Radiation: CuKα1 - 1.5406 Å.  b Fixed slit intensity. | | | | |

1. (informative)  
     
   Interferences on quartz and cristobalite diffraction patterns

Potential mineral interferences with the principal diffraction peaks of quartz and cristobalite are represented in Tables B.1 and B.2 respectively, where the number of dots is an assessment of the severity of the interference. Interference assessment is based on theoretical binary mixtures of CS phase with pure minerals. For each mineral, three mixtures are represented: 80% quartz (or cristobalite) and 20% interfering mineral, 50%-50%, and 20%-80%. Minerals not interfering with quartz or cristobalite peaks are listed in the note of each table. Examples of interferences are shown in Figure B.1.

**Key**

|  |  |
| --- | --- |
| I | intensity (counts) |
| °2θ | diffraction angle |

**Figure B.1 — Examples of diffraction interferences on the pattern of primary peak of quartz (Cu radiation), in binary mixtures 20% quartz – 80% interfering mineral. A) Maghemite (•). B) Anorthite (••). C) Tremolite (•••). D) Gibbsite (••••). E) Illite (•••••). F) Barite (•••••). The thick grey line represents the diffraction pattern, the solid black line represents quartz (101) component, and the dotted line the interfering mineral diffraction pattern component.**

**Table B.1 — Mineral interferences with three principal diffraction peaks of quartz**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Mineral** | **Quartz** | | | | | | | | |
| Qz1 (101) | | | Qz2 (100) | | | Qz3 (112) | | |
| *80%Qz* | *50%Qz* | *20%Qz* | *80%Qz* | *50%Qz* | *20%Qz* | *80%Qz* | *50%Qz* | *20%Qz* |
| Albite |  | **•** | **••** |  |  |  | **•** | **•••** | **•••••** |
| Anhydrite |  |  |  |  |  |  | **•** | **•** | **•** |
| Ankerite |  |  |  |  |  |  | **•••** | **•••••** | **•••••** |
| Anorthite |  | **•** | **••** |  |  | **•** | **••** | **••** | **•••** |
| Aragonite | **•** | **••** | **••** |  | **•** | **••** | **•••** | **•••••** | **•••••** |
| Barite | **••** | **•••••** | **•••••** | **•** | **••** | **•••** |  |  |  |
| Biotite | **•** | **••** | **•••••** |  |  |  |  |  |  |
| Boehmite |  |  |  |  |  |  |  | **•** | **•** |
| Butlerite |  |  |  |  |  |  | **•** | **••** | **••** |
| Celestine | **••** | **•••** | **••••** | **••** | **•••** | **•••••** |  |  |  |
| Chamosite |  |  | **•** | **•** | **•** | **•••** | **•** | **•••** | **•••••** |
| Chlorapatite |  |  |  | **•** | **••** | **••** | **•••** | **•••••** | **•••••** |
| Chlorite |  |  |  | **••** | **••** | **•••** | **••** | **•••••** | **•••••** |
| Clinochlore |  | **•** | **•** | **•** | **••** | **•••••** | **•** | **•••** | **•••••** |
| Cordierite | **•** | **•••** | **•••••** |  | **•** | **••** | **••** | **••••** | **•••••** |
| Crandallite |  |  |  |  |  |  | **•** | **•** | **••** |
| Diaspore |  |  |  |  |  |  | **•** | **••** | **•••••** |
| Dolomite |  |  |  |  |  |  | **••** | **••** | **•••** |
| Fluorapatite |  |  |  |  |  |  | **••** | **•••** | **••••** |
| Gibbsite | **•** | **••** | **••••** | **••** | **••** | **••** | **••** | **•••••** | **•••••** |
| Goethite |  | **••** | **••** | **•••** | **•••** | **•••••** | **••** | **••** | **•••** |
| Graphite | **••** | **•••••** | **•••••** |  |  |  | **•** | **•** | **•** |
| Gypsum |  |  |  | **•••••** | **•••••** | **•••••** | **•** | **•••** | **•••••** |
| Hausmannite |  |  |  |  |  |  | **•** | **•••** | **•••••** |
| Illite | **•** | **••** | **•••••** | **•** | **••** | **••** |  |  |  |
| Jarosite |  |  |  |  |  |  | **••••** | **•••••** | **•••••** |
| Kaolinite |  |  | **•** | **•** | **•** | **••** |  |  |  |
| Lepidocrocite | **•** | **••** | **••** |  |  |  |  |  |  |
| Maghemite |  |  | **•** |  |  |  | **•** | **•••** | **•••••** |
| Microcline | **••** | **•••** | **••••** | **•••** | **••••** | **•••••** | **••** | **••** | **••••** |
| Montmorillonite |  |  |  | **••••** | **•••••** | **•••••** |  |  |  |
| Mullite | **•** | **•** | **••** |  |  |  | **•** | **•** | **••** |
| Muscovite | **•** | **••** | **•••••** | **•** | **•••** | **••••** |  |  | **••** |
| Orthoclase | **••** | **•••** | **•••** | **••••** | **•••••** | **•••••** | **•** | **••** | **••** |
| Pyrophyllite |  |  |  | **•••** | **•••••** | **•••••** |  |  | **••** |
| Siderite |  |  |  |  |  |  | **•** | **•** | **••** |
| Sillimanite | **•** | **•••** | **•••••** |  |  |  | **••** | **••** | **••** |
| Talc |  |  |  | **••** | **••** | **•••** |  | **•** | **••** |
| Tremolite | **••** | **••** | **•••** | **••** | **••** | **•••** |  | **•** | **•••** |
| Tridymite |  | **•** | **•** | **••** | **••••** | **•••••** |  | **•** | **••** |
| Vaterite | **•** | **••** | **••** | **•** | **•••** | **•••••** | **•••••** | **•••••** | **•••••** |
| Wollastonite | **•** | **••** | **•••••** |  |  |  | **••** | **••••** | **•••••** |
| Zircon | **••** | **•••** | **••••** |  |  | **•** |  |  |  |
| NOTE   Interference increases from **•** to **•••••**  Minerals with XRD patterns not overlapping those of quartz:  Aluminium, Alunite, Anatase, Bunsenite, Calcite, Chlorargyrite, Corundum, Cristobalite, Fluorite, Grossular, Halite, Hematite, Ilmenite, Magnetite, Perovskite, Pyrite, Pyrolusite, Rutile, Silver, Sphalerite, Spinel, Zinc | | | | | | | | | |

**Table B.2 — Mineral interferences with two principal diffraction peaks of cristobalite**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Mineral** | **Cristobalite** | | | | | |
| Cr1 (101) | | | Cr3 (102) | | |
| *80%Cr* | *50%Cr* | *20%Cr* | *80%Cr* | *50%Cr* | *20%Cr* |
| Albite | **•** | **••** | **•••••** | **•** | **•••** | **•••••** |
| Alunite |  |  |  | **••** | **•••** | **••••** |
| Ankerite |  |  |  | **•** | **••** | **••** |
| Anorthite | **•** | **••** | **•••** | **••** | **••••** | **•••••** |
| Aragonite |  |  |  | **•** | **••** | **••••** |
| Barite |  |  |  | **•••••** | **•••••** | **•••••** |
| Butlerite |  |  |  | **•** | **•••** | **•••••** |
| Calcite |  |  |  | **•** | **••** | **•••••** |
| Chamosite |  | **•** | **••** | **•** | **••••** | **•••••** |
| Chlorapatite |  |  |  | **•••••** | **•••••** | **•••••** |
| Chlorite |  |  |  | **••** | **•••** | **•••••** |
| Clinochlore |  | **•** | **••** | **•** | **•••** | **•••••** |
| Cordierite | **•** | **•••** | **••••** |  | **•** | **•** |
| Crandallite |  |  |  | **•** | **•••** | **•••••** |
| Diaspore | **••** | **••** | **•••** |  |  |  |
| Dolomite |  | **•** | **•** | **•••** | **••••** | **•••••** |
| Fluorapatite | **•** | **•** | **•** | **••** | **••** | **•••** |
| Gypsum |  |  |  | **••••** | **•••••** | **•••••** |
| Halite |  |  |  | **••••** | **•••••** | **•••••** |
| Hausmannite |  |  |  | **••** | **•••** | **••••** |
| Illite | **•** | **•** | **••** | **••** | **•••** | **•••••** |
| Jarosite |  |  |  | **•••** | **•••** | **•••••** |
| Kaolinite |  |  | **••** | **•** | **•••** | **•••••** |
| Microcline |  |  |  | **•** | **•** | **••** |
| Mullite |  |  |  | **•** | **••** | **••** |
| Muscovite |  | **•** | **••** | **••** | **•••** | **•••••** |
| Orthoclase |  |  |  | **•** | **•** | **••** |
| Pyrophyllite | **•** | **••** | **•••••** |  |  |  |
| Spinel |  |  |  | **••••** | **•••••** | **•••••** |
| Talc | **•** | **••** | **••** |  |  |  |
| Tremolite |  |  | **•** |  |  | **•** |
| Tridymite | **••** | **•••** | **••••** |  |  | **•** |
| Wollastonite |  | **•** | **••** |  |  |  |
| NOTE   Interference increases from **•** to **•••••**  Minerals with XRD patterns not overlapping those of cristobalite:  Aluminium, Anatase, Anhydrite, Biotite, Boehmite, Bunsenite, Celestine, Chlorargyrite, Corundum, Fluorite, Gibbsite, Goethite, Graphite, Grossular, Hematite, Ilmenite, Lepidocrocite, Maghemite, Magnetite, Montmorillonite, Perovskite, Pyrite, Pyrolusite, Quartz, Rutile, Siderite, Sillimanite, Silver, Sphalerite, Vaterite, Zinc, Zircon | | | | | | |

1. (informative)  
     
   Sample treatment strategies
   1. Generalities

Pre-concentration of crystalline silica prior to XRPD analysis is desirable if the crystalline silica is present in small amounts. However, is not advisable for limited sample amounts and every care must be taken to ensure the validity and credibility of the pre-concentration procedure [12].

Treatment is usually performed on the ground sample. For some samples, it may be possible to use some form of chemical treatment to concentrate crystalline silica or to remove potentially interfering phases. It is obviously essential that such treatment does not remove any crystalline silica present or change its form.

Chemical treatment that add complexity of experimental work, produce limited success and introduce systematic experimental error cannot be recommended.

* 1. Acid soluble components: calcite, dolomite, gypsum, iron oxides

Calcite, dolomite, gypsum, iron and its oxides can be removed with the use of dilute hydrochloric acid (HCl) for a short time.

Iron has a high absorption for copper X-ray radiation, so its removal is beneficial if the sample is mostly hematite, magnetite or iron metal. Iron can be removed by treating the sample with a warm solution (e.g. 60 °C) of hydrochloric acid – water (1+2) for longer periods (e.g. 2 hours). The mixture is filtered through a pulp pad, which is then ignited [8].

Dilute acetic acid is often preferred over hydrochloric acid to dissolve the carbonates in limestone and sediments. A solution is prepared adding 1 part acetic acid to 4 parts distilled water. The solution is poured on the powdered sample placed in a beaker. The operation is repeated until the suspension no longer effervesces.

* 1. Silicates (mullite)

Silicates such as mullite (3Al2O3.2SiO2), which give a diffraction peak very close to the quartz primary peak, are removed by fusing the sample with analytical-reagent grade potassium hydrogen sulphate and dissolving the melt in hot water to which a few millilitres of hydrochloric acid - water (1 + 2) have been added. The solution is filtered through a pulp pad, which is then ignited, and any quartz is left as a residue [8].

* 1. Clay minerals

Kaolinite is a common interference in mineral samples, which can decompose in temperatures as low as 450 °C. For other clay minerals that are polymorphous with kaolinite, like nacrite and dickite the temperature for decomposition may be as high as 650 ± 50 °C, although it might require a temperature of 800 °C for their complete removal. Care should be taken when heating quartz to temperatures higher than 800 °C for any length of time. Although the conversion temperature from quartz to cristobalite is about 1100 °C partial conversion is observed in some samples in temperatures above 800 °C. Some clay samples from industrial sources may also contain calcite. In this case, calcite should be removed with dilute acid, following paragraph C.4, before heating samples in a furnace. The formation of wollastonite from the reaction with calcite and silica can occur at temperatures as low at 500 °C. Use a furnace temperature within ± 50°C appropriate for the clay matrix.

* 1. Vermiculite

Vermiculite is a hydrous phyllosilicate mineral, which is imported into many countries and can contain traces of chrysotile asbestos and crystalline silica as a contaminant. Vermiculite has several minor diffraction peaks close to the primary (101) and secondary (100) quartz reflections. Vermiculite interference can be reduced by heating the mineral overnight in a furnace at 600 °C, refluxing for 1 h in 2 N sulphuric acid, centrifuging with water and filtration [13].

* 1. Coal and similar carbon based materials

Some carbon based components (e.g. anthracite or graphite) and organic matter can be removed by ashing in a furnace at about 800 ± 50 °C. However, the heating process can potentially oxidise other components in the sample (e.g. iron) and add to the complexity of the analysis.

1. (informative)  
     
   Examples of analyses
   1. External standard method – deposition on filter
      1. Calibration curves for quartz determination
         1. Calibration filters preparation

- A plan with the target weights of quartz reference material to be deposited on the filters was prepared (Table D.1), where a 4,5 mg maximum weight of quartz was set. The preparation of two suspensions was planned. The aliquots of suspension to be withdrawn were calculated taking into account the weights of quartz reference material (10 and 50 mg) to be poured into the two 500 mL 2-propanol suspensions.

**Table D.1 — Example of a plan for the preparation of 14 calibration filters in the range 0,01 to 4,5 mg from two suspensions of quartz reference material in 2-propanol**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Suspension No. 1** | | | **Suspension No. 2** | | |
| **Specimen**  **No.** | Reference Qz weight in the suspension (mg) | *Volume of the suspension in the flask (mL)* | **Specimen**  **No.** | Reference Qz weight in the suspension (mg) | *Volume of the suspension in the flask (mL)* |
| 1 | 500 | 50 | 500 |
| Reference Qz weight in the calibration specimen (mg) | Volume for the aliquot (mL) | Reference Qz weight in the calibration specimen (mg) | Volume for the aliquot (mL) |
| 1 | 0,01 | 5 | 7 | 0,5 | 5 |
| 2 | 0,02 | 10 | 8 | 1 | 10 |
| 3 | 0,03 | 15 | 9 | 1,5 | 15 |
| 4 | 0,05 | 25 | 10 | 2 | 20 |
| 5 | 0,07 | 35 | 11 | 2,5 | 25 |
| 6 | 0,1 | 50 | 12 | 3 | 30 |
|  | | | 13 | 3,5 | 35 |
| 14 | 4,5 | 45 |

- Each blank silver filter was weighed to the nearest μg according to ISO 15767, then XRD analysed for the most intense reflection of silver, .

- Two suspensions were prepared by first weighing 1 and 50 mg of a quartz reference material to the nearest 0,01 mg, then quantitatively transferring them to 500 mL volumetric flasks, and bring each of them to volume using 2-propanol.

- The powder in the 2-propanol was dispersed with an ultrasonic probe or bath for 3 min. The suspension was immediately moved to a magnetic stirrer without heat, and a stirring bar was added into the flask.

- A silver filter was mounted on the vacuum filtration assembly, and 2-3 mL of 2-propanol were poured on the filter.

- The stirrer was turned off and the suspension was shaken by hand. An aliquot was immediately withdrawn from about the centre of the suspension, and transferred from the pipette to the glass funnel. The volume was ejected from the pipette into the glass funnel. The sides of the funnel were not washed after the deposit was in place, to avoid rearrangement of particles on the analysis filter. The same vacuum filtration assembly used for the calibration, or one with very similar dimensions, was used for all the subsequent analyses of unknown samples.

Note 1: The diameter of the glass funnel and suction area below the filter have an influence on the area of deposition of the specimen and hence the sensitivity of the calibration. Different vacuum filtration assemblies can have different dimensions.

Note 2: The volume of the glass funnel is typically 20 mL, therefore when the volume of the aliquot to be withdrawn is more than 20 mL, the solution in excess may be carefully poured into the glass funnel when the vacuum is applied.

- Vacuum was applied and the suspension rapidly filtered. Vacuum was left on until the filter was thoroughly dry (3-4 min), then the filter was removed.

- The filter was reweighed to determine the deposit weight (), that in most cases resulted slightly different from its target value.

- The correction for the purity of quartz in the reference material (=93,7%) was applied, obtaining the weight of quartz in the calibration filter, (Table D.2):

* + - 1. Diffraction analyses

- A silicon polycrystalline reference disc was analysed at the beginning and ending of the analysis session, measuring the primary peak of silicon, to determine the drift of diffraction intensity over time, and its average intensity was recorded as the reference value, , to be used in the analysis of unknown specimens (Table D.2).

- Each calibration filter was mounted in turn in the diffractometer, and the diffraction intensities of the three most intense reflections j of quartz were measured, together with the intensity of the silver primary peak (Table D.2).

**Table D.2 — Example of weighing and analysis of calibration filters prepared according to the plan provided in Table D.1**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Filter No.** | ***Before deposition*** | | ***After deposition*** | | | | | | | | | |
| weight | IAg1,B | weight | WQz | IAg1 | 2θAg1 | IQz1 | 2θQz1 | IQz2 | 2θQz2 | IQz3 | 2θQz3 |
| mg | counts·° | mg | mg | counts·° | *°* | counts·° | ° | counts·° | ° | counts·° | ° |
| 1 | 200,875 | 24923 | 200,886 | 0,010 | 24539 | 38,149 | 89 | 26,663 | 17 | 20,885 | n.d. | - |
| 2 | 214,540 | 25967 | 214,558 | 0,017 | 25837 | 38,055 | 147 | 26,570 | 29 | 20,803 | n.d. | - |
| 3 | 206,047 | 25165 | 206,085 | 0,036 | 24954 | 38,080 | 324 | 26,590 | 69 | 20,818 | 36 | 50,041 |
| 4 | 207,726 | 23467 | 207,780 | 0,051 | 22552 | 38,196 | 337 | 26,720 | 101 | 20,929 | 35 | 50,180 |
| 5 | 204,686 | 22543 | 204,768 | 0,077 | 22285 | 38,198 | 562 | 26,718 | 146 | 20,924 | 65 | 50,167 |
| 6 | 204,693 | 23708 | 204,797 | 0,097 | 23386 | 38,172 | 690 | 26,694 | 157 | 20,911 | 110 | 50,144 |
| 7 | 191,920 | 24618 | 192,456 | 0,502 | 24253 | 38,119 | 5654 | 26,642 | 1259 | 20,856 | 674 | 50,010 |
| 8 | 186,754 | 25511 | 187,798 | 0,978 | 23643 | 38,090 | 10394 | 26,604 | 2383 | 20,816 | 1258 | 50,042 |
| 9 | 193,705 | 23253 | 195,659 | 1,831 | 20526 | 38,070 | 17761 | 26,590 | 4074 | 20,800 | 2268 | 50,061 |
| 10 | 200,178 | 26057 | 202,240 | 1,932 | 22507 | 38,060 | 19648 | 26,579 | 4549 | 20,794 | 2566 | 50,055 |
| 11 | 193,930 | 26574 | 196,879 | 2,763 | 21435 | 37,940 | 29582 | 26,460 | 6583 | 20,680 | 3740 | 49,923 |
| 12 | 208,597 | 25685 | 211,697 | 2,905 | 19737 | 38,063 | 27489 | 26,583 | 6344 | 20,797 | 3372 | 50,040 |
| 13 | 200,448 | 22607 | 204,458 | 3,757 | 16802 | 38,090 | 31425 | 26,610 | 7015 | 20,820 | 3928 | 50,060 |
| 14 | 216,560 | 22982 | 221,488 | 4,618 | 15977 | 38,090 | 36438 | 26,610 | 8934 | 20,820 | 4858 | 50,060 |
| Silicon polycrystalline disc: | | | XQz = 93,7% | | 2θAg1,ref | | 2θQz1,ref | | 2θQz2,ref | | 2θQz3,ref | |
| Ibeginning= | | 19005 | IM°= | 19039 | average= | 38,098 | average= | 26,617 | average= | 20,832 | average= | 50,065 |
| Iending= | | 19073 | st. dev.= | 0,067 | st. dev.= | 0,068 | st. dev.= | 0,066 | st. dev.= | 0,071 |

**Table D.3 — Corrected intensities and reference values for the data of Table D.2.**

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Filter**  **No.** | ***T*** | ***fabQz1*** | ***fabQz2*** | ***fabQz3*** | ***IQz1C*** | ***IQz2C*** | ***IQz3C*** | **IQz2rel** | **IQz3rel** | **FWHMQz1** | **AsQz1** | **FWHMQz2** | **AsQz2** |
| counts·°2θ | | | °2θ | °2θ |
| 1 | 0,985 | 1,011 | 1,014 | 1,006 | 90 | 18 | n.d. | 19,5 | - | 0,141 | 0,90 | 0,111 | 0,71 |
| 2 | 0,995 | 1,004 | 1,005 | 1,002 | 147 | 30 | n.d. | 20,0 | - | 0,145 | 0,88 | 0,180 | 1,85 |
| 3 | 0,992 | 1,006 | 1,008 | 1,003 | 326 | 70 | 37 | 21,4 | 11,2 | 0,144 | 0,95 | 0,140 | 1,17 |
| 4 | 0,961 | 1,028 | 1,036 | 1,015 | 346 | 105 | 36 | 30,2 | 10,3 | 0,145 | 0,94 | 0,177 | 0,67 |
| 5 | 0,989 | 1,008 | 1,010 | 1,004 | 566 | 148 | 66 | 26,1 | 11,6 | 0,151 | 0,98 | 0,154 | 1,07 |
| 6 | 0,986 | 1,010 | 1,012 | 1,005 | 696 | 159 | 111 | 22,9 | 15,9 | 0,152 | 1,07 | 0,150 | 1,29 |
| 7 | 0,985 | 1,011 | 1,014 | 1,006 | 5714 | 1276 | 678 | 22,3 | 11,9 | 0,155 | 0,94 | 0,150 | 1,08 |
| 8 | 0,927 | 1,055 | 1,070 | 1,030 | 10964 | 2550 | 1295 | 23,3 | 11,8 | 0,154 | 0,98 | 0,145 | 1,12 |
| 9 | 0,883 | 1,091 | 1,117 | 1,049 | 19378 | 4550 | 2379 | 23,5 | 12,3 | 0,162 | 1,04 | 0,154 | 1,17 |
| 10 | 0,864 | 1,107 | 1,138 | 1,058 | 21759 | 5177 | 2713 | 23,8 | 12,5 | 0,148 | 0,95 | 0,140 | 1,11 |
| 11 | 0,807 | 1,160 | 1,206 | 1,085 | 34317 | 7943 | 4059 | 23,1 | 11,8 | 0,148 | 0,94 | 0,142 | 1,08 |
| 12 | 0,768 | 1,198 | 1,257 | 1,105 | 32940 | 7972 | 3726 | 24,2 | 11,3 | 0,150 | 0,98 | 0,139 | 1,07 |
| 13 | 0,743 | 1,225 | 1,292 | 1,119 | 38499 | 9061 | 4395 | 23,5 | 11,4 | 0,167 | 1,06 | 0,163 | 1,19 |
| 14 | 0,695 | 1,280 | 1,364 | 1,147 | 46632 | 12184 | 5570 | 26,1 | 11,9 | 0,171 | 1,09 | 0,168 | 1,23 |
| Reference values (average): | | | | | | | | 23,6 | 12,0 | 0,152 | 0,98 | 0,151 | 1,13 |
| Standard deviation: | | | | | | | | 2,7 | 1,3 | 0,009 | 0,06 | 0,018 | 0,27 |

* + - 1. Calculations

- The average values of the diffraction parameters described in 8.4.2 (line position , full width at half maximum , and asymmetry were calculated for the three most intense lines j of quartz (Table D.3). The average position of the primary peak of silver was also calculated (Table D.2).

- For each calibration filter and peak j, the diffraction intensity corrected for absorption, were calculated as (Table D.3):

where

is the correction factor for absorption;

is the transmittance;

.

Note: The correction for absorption is not necessary for specimens with mass lower than approximately 1 mg [14].

- The following relative intensities were calculated (Table D.3):

and

The average relative intensities from all the calibration specimens were recorded as reference values ( and ) to be used in the analysis of unknown specimens.

* + - 1. Calibration lines construction

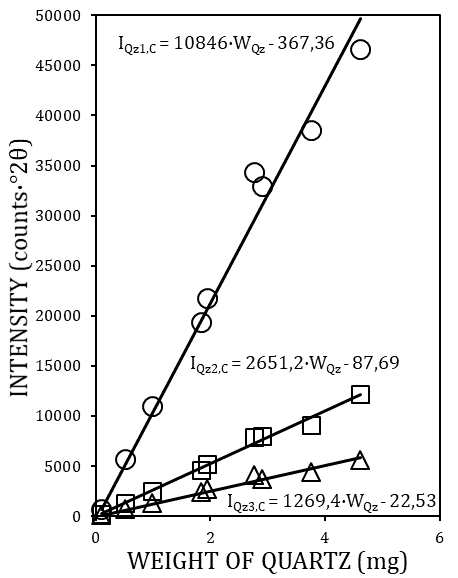
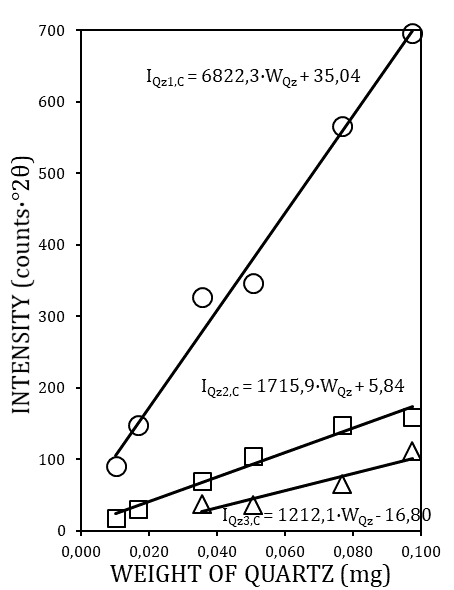
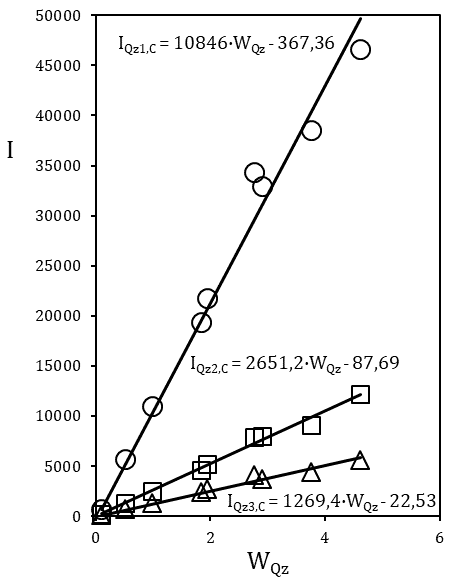
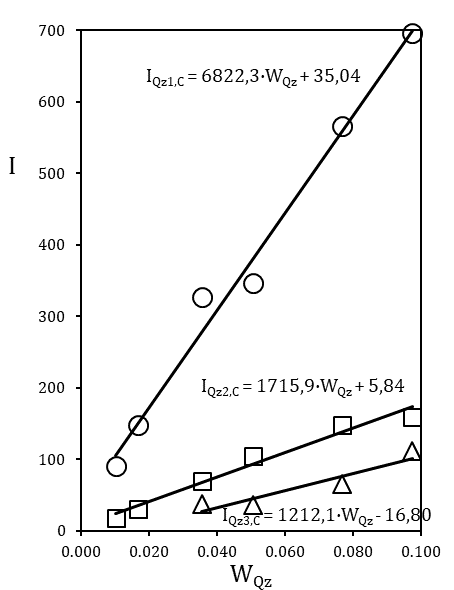
- The calibration lines for the range 0,01-0,1 mg of quartz was constructed for the three major diffraction reflections (Figure D.1 left). The linear regression analysis is based on the equation:

where

is the slope of the line for the range 0,01-0,1 mg;

is the intercept of the line for the range 0,01-0,1 mg.

- The calibration lines for the range 0,1-4,6 mg of quartz were calculated for the three major diffraction reflections. Each trend line was forced through the point with coordinates =0,1 mg and . Results are shown in Figure D.1 right.



**Key**

|  |  |
| --- | --- |
| I | intensity (counts·°) |
| WQz | weight of quartz (mg) |

**Figure D.1 — Example of instrument calibration for the three most intense reflections of quartz (data in Tables D.2-3), by using two separate lines between 0,01-0,1 mg (left) and 0,1-4,6 mg (right) of quartz**

* + 1. Determination of quartz in a sample
       1. Number of sample specimens to be analysed

- Since the quantity of sample in a specimen deposited on a filter is small, a single specimen might not be sufficiently representative of the sample. Therefore, it is a good practise to analyse at least two specimens. If the percent weight fractions resulting from the two analyses are within a 10% relative difference ∆, their average value is adopted as the result.

* + - 1. Specimen preparation

- Before depositing the specimen on a blank silver filter, the filter was XRD analysed for the most intense reflection of silver, , and then weighed to the nearest μg (Table D.4).

- The bulk material was crushed and ground to approximately the same grain size of the quartz reference material deposited on the calibration filters (see section 7). The specimen powder was deposited on the silver filter (see section 7.7), weighed again, and finally the specimen weight, =1,947 mg, was calculated (Table D.4).

* + - 1. Diffraction analysis

- The primary diffraction line of silicon from the silicon polycrystalline reference disc was analysed at the beginning and ending of the analysis session (Table D.4).

- The specimen filter was mounted in the diffractometer. XRD scans were carried out in profile ranges of three most intense reflections of quartz, and of the primary peak of silver. Results are shown in Figure D.2.

**Key**

|  |  |
| --- | --- |
| I | intensity (counts) |
| °2θ | diffraction angle |

**Figure D.2 — Diffraction patterns for the analysed specimen. The y-axis is represented in logarithmic scale to better visualize background fluctuations and potential interference.**

**Table D.4 — Results for gravimetric and XRD analyses in the specimen, and correction factors**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Filter**  No. | ***Before deposition*** | | ***After deposition*** | | | | | | | | | |
| weight | IAg1,B | weight | WQz | IAg1 | 2θAg1 | IQz1 | 2θQz1 | IQz2 | 2θQz2 | IQz3 | 2θQz3 |
| mg | counts·° | mg | mg | counts·° | *°* | counts·° | ° | counts·° | ° | counts·° | ° |
| x | 200,910 | 24834 | 201,533 | 1,947 | 21167 | 38,175 | 3226 | 26,691 | 874 | 20,911 | 290 | 50,181 |
| ISi1,beginning= | | 18054 | IM= | 18078 | Silver primary peak 2θ position, reference value: 2θAg1,ref = 38,098° | | | | | | | |
| ISi1,ending= | | 18101 | Diffraction pattern displacement: ∆2θ = -0,077° | | | | | | | |
| Reference value: | | | IM°= | 19039 | Transmittance: T = 0,852 | | | | | | | |
| Correction factor: | | | *fem*= | 1,053 | Correction factors: *fab,Qz1* = 1,118; *fab,Qz2* = 1,151; *fab,Qz3* = 1,063 | | | | | | | |

**Table D.5 — Results for quartz reflections in the specimen**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Filter**  No. | ***2θQz1,C*** | ***2θQz2,C*** | ***2θQz3,C*** | **IQz2rel** | **IQz3rel** | **FWHMQz1** | **AsQz1** | **FWHMQz2** | **AsQz2** |
| ° | | | ° | ° |
| x | 26,614 | 20,834 | 50,104 | 27,9 | 8,5 | 0,166 | 1,17 | 0,194 | 1,12 |
| Reference values: | 26,617 | 20,832 | 50,065 | 23,6 | 12,0 | 0,152 | 0,98 | 0,151 | 1,13 |

* + - 1. Quartz identification

- The line position of the primary peak of silver, , was compared with its reference value, (Table D.4). The diffraction pattern displacement, ∆2θ, was calculated as:

Note 1: A slight displacement of the diffraction pattern generally occurs, because it is difficult to obtain the specimen surface exactly level with the specimen holder. A rigorous displacement correction algorithm, where the displacement is a function of the angular position 2θ, is generally included in any dedicated software, but a simplified linear shift of the entire diffraction pattern generally produces an acceptable approximation.

- The diffraction pattern (Figure D.2) was visually inspected, and peaks of quartz identified and measured (Table D.4). Line positions of the three most intense lines *j* of quartz were corrected for displacement (Table D.5):

Had quartz not been identified in the diffraction pattern, the analysis result would have been reported as <LOQ in the test report.

- Quartz diffraction peaks were visually evaluated for double peaks, shoulders, and other anomalies. The primary peak of quartz (101) appeared to be affected by interference (Figure D.2), while the secondary peak (100) resulted free from interference.

- The corrected line positions , the full widths at half maximum , and the asymmetries were compared with their reference values found for pure quartz in calibration filters (Figure D.5). The relative intensities were calculated as:

* , and .

Their values, shown in Table D.5, did not agree with their reference values. The interference was evaluated as significant (relative difference between measured and reference values >15%), and ascribed to the primary peak of quartz.

Based on all the observations described above, the secondary peak of quartz was chosen for quantification.

* + - 1. Calculations for quantitative determination

- The measured quartz diffraction intensity (Table D.4) was corrected for absorption and for the drift in XRD radiation intensity over time:

* =1,151 · 1,053 · 874 = 1059 counts·°2θ

where

|  |  |  |
| --- | --- | --- |
|  |  | is the correction factor for absorption (equation given in Annex D.1.1.3); |
|  |  | is the correction factor for the drift in XRD radiation intensity: . |

- The weight of quartz in the specimen was calculated according to the appropriate calibration line (0,1-4,6 mg, Figure D.1 right):

* (1059 + 87,69) / 2651,2 = 0,433 mg

- The percent weight fraction of quartz in the specimen was calculated as:

* (0,433/1,949)·100 = 22,2
  + - 1. Second specimen analysis and result for the percent weight fraction of quartz in the sample

- A second specimen was prepared and analysed, following the same procedure described in Annex D.1.2.2 to D.1.2.5. The specimen percent weight fraction was calculated as 21,1.

- The percent weight fraction of quartz in the sample, , was calculated as the average between the values found for the two specimens:

* (22,2 + 21,1) / 2 = 21,65

The relative difference between the two values was within the accuracy limit of the method:

* (22,2 - 21,1) / 21,65 = 5,2%
  1. Internal standard method
     1. Reference Intensity Ratio (RIR) approach
        1. Determination of RIR for quartz, using corundum as internal standard

- Three mixtures of ~50% quartz (*Qz*) reference material and ~50% pure corundum (*Crn*) internal standard were prepared according to the procedure given in section 7.6 (Table D.6).

- The specimen holders used for the analyses were tested and proved to contain 1,90-1,95 g of powder, then a slight heavier weight (2,00 g) was chosen as the target weight for the mixture to be prepared. Therefore, the weight of both corundum and quartz reference materials in the mixture, and , was planned to be approximately 1,00 g.

- Three calibration specimens were prepared, mounted on the diffractometer and analysed.

* The diffraction intensities , , and were measured (results for are shown in Table D.6).
* The second most intense line of corundum (104) at 35,07° 2θ (Cu-anode), indicated as *Crn2*, was chosen as the internal standard reference line, and measured (results for are shown in Table D.6).
* The line position *2θ* of the maximum, the Full Width at Half Maximum *FWHM*, and the asymmetry *As* of each diffraction line were also recorded.

- The specimens were disrupted, prepared again from the same mixtures, and analysed. The procedure was repeated obtaining 9 sets of data (Table D.6).

- The average values of diffraction intensities of the three most intense lines of quartz, their relative intensities (an automatic divergence slit was used in the incident beam), and the ratio between third and second most intense peaks, were recorded as reference values:

* 31953 counts·°2θ 100
* 6411 counts·°2θ 20
* 3923 counts·°2θ 12
* 61%

The average values of *2θ*, *FWHM*, and *As* were also calculated for each diffraction line, and recorded as reference values.

* For all the 9 sets of data, the Intensity Ratio, , of each line of quartz, was calculated as:
* The was calculated as the arithmetic average of all the values (Table D.6):

**Table D.6 — Calculation of Reference Intensity Ratio for the primary peak of quartz (*RIRQz1*). Intensities values are for the peaks *ij*, where *i* is quartz or corundum and *j* is the primary peak for quartz or secondary peak for corundum**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Mixture**  *No.* | **Mineral** | **Weight** | **Weight percent** | **Specimen**  *No.* | **Mineral** | **Intensity** | *IRQz1* | *RIRQz1* | *ST.DEV* |
| *Wi* | *W%i* | *Iij* |
| *mg* | *%* | *counts·°* |
| 1 | Quartz | 1,00002 | 50,04 | 1A | Quartz | 33468,4 | 5,874 | 5,782 | 0,459 |
| Corundum | 5687,5 |
| 1B | Quartz | 31788,3 | 5,470 |
| Corundum | 0,99831 | 49,96 | Corundum | 5801,4 |
| 1C | Quartz | 31055,3 | 5,358 |
| Corundum | 5786,2 |
| 2 | Quartz | 1,00024 | 50,10 | 2A | Quartz | 34876,4 | 6,808 |
| Corundum | 5103,3 |
| 2B | Quartz | 32504,1 | 5,952 |
| Corundum | 0,99641 | 49,90 | Corundum | 5439,9 |
| 2C | Quartz | 31833,7 | 5,574 |
| Corundum | 5688,9 |
| 3 | Quartz | 1,00036 | 49,94 | 3A | Quartz | 33816,5 | 6,060 |
| Corundum | 5593,3 |
| 3B | Quartz | 30522,5 | 5,518 |
| Corundum | 1,0027 | 50,06 | Corundum | 5544,7 |
| 3C | Quartz | 30639,5 | 5,424 |
| Corundum | 5662,6 |

* + - 1. Determination of quartz in a sample

- A preliminary diffraction scan was carried out on a specimen of sample unmixed with any internal standard, for quartz identification. The three most intense peaks of quartz were identified in their experimental diffraction patterns. A visual inspection of the pattern did not point out to any anomaly on the shapes of the three peaks of quartz. The following intensities were measured, and the relative intensities calculated:

* 24023 counts·°2θ 100
* 4658 counts·°2θ 19
* 3036 counts·°2θ 13

Line *Qz1* did not result affected by interferences, and was chosen to represent the sample in the quantitative analysis.

A diffraction scan on the same specimen, in the angular range of the secondary peak of corundum did not reveal any peak.

- A specimen with a mixture of ~50% sample (*s*) and ~50% pure corundum (*Crn*) internal standard was prepared:

* sample weight: 1,00115 g
* corundum weight: 0,99996 g
* sample percent weight fraction 50,05
* corundum percent weight fraction: 49,97.

- The specimen was analysed in the angular ranges of the primary peak of quartz and secondary peak of corundum. The following intensities were measured:

* 11976 counts·°2θ
* 4323 counts·°2θ

- The percent weight fraction of quartz in the sample, , was determined:

* 47,9

**Table D.7 — Example of results of a calibration exercise for the calibration of primary peak of quartz (from [8])**

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Specimen** | **Percent weight fraction in the mixtures** | | | *W%RQz* | **XRPD Intensity** | | **Intensity Ratio** |
| **Quartz** | **Nickel(II) oxide** | **Diluent** | *IQz1* | *IBun1* | *IRQz1* |
| No. | % | % | % | % | counts·° | counts·° |
| 1 | 6,15 | 50,00 | 43,85 | 12,3 | 4278 | 15011 | 0,285 |
| 2 | 12,30 | 50,00 | 37,70 | 24,6 | 8204 | 12799 | 0,641 |
| 3 | 13,90 | 50,00 | 36,10 | 27,8 | 9445 | 13435 | 0,703 |
| 4 | 17,80 | 50,00 | 32,20 | 35,6 | 12831 | 16242 | 0,790 |
| 5 | 22,90 | 50,00 | 27,10 | 45,8 | 15073 | 14206 | 1,061 |
| 6 | 27,20 | 50,00 | 22,80 | 54,4 | 19589 | 18021 | 1,087 |
| 7 | 32,50 | 50,00 | 17,50 | 65,0 | 23443 | 17937 | 1,307 |
| 8 | 35,55 | 50,00 | 14,45 | 71,1 | 25215 | 17153 | 1,470 |
| 9 | 39,90 | 50,00 | 10,10 | 79,8 | 27002 | 15608 | 1,730 |
| 10 | 42,15 | 50,00 | 7,85 | 84,3 | 30037 | 16495 | 1,821 |
| 11 | 47,00 | 50,00 | 3,00 | 94,0 | 31325 | 16988 | 1,844 |
| 12 | 50,00 | 50,00 | 0,00 | 100,0 | 34488 | 17331 | 1,990 |

* + 1. Calibration graph approach
       1. Construction of a calibration line for quartz, using nickel(II) oxide as internal standard

- Twelve mixtures of quartz (*Qz*) reference material, pure nickel(II) oxide (bunsenite - *Bun*) internal standard, and a diluent powder (γ-aluminium(III) oxide - *diluent*) were prepared according to the procedure given in section 7.6.

- The weight of each mixture was ~2 g. The internal standard weight fraction was a fixed value in all the mixtures, 50. The quartz weight fraction in the 12 mixtures increased between approximately 6% and 50%. The remaining percent weight fraction was filled with the diluent powder: . The weighing accuracy was within 0,0001 g. The percent weight ratio between quartz and internal standard in each mixture was calculated as:

- A calibration specimen from each mixture was prepared, mounted on the diffractometer and analysed (data for *Qz1* are shown in Table D.7).

* The diffraction intensities , , and were measured.
* The most intense line of bunsenite (200) at 43,10° 2θ (Cu-anode), indicated as *Bun1*, was chosen as the internal standard reference line, and measured.
* The intensity ratios were calculated for each specimen:
* The line position *2θ* of the maximum, the Full Width at Half Maximum *FWHM*, and the asymmetry *As* of each diffraction line were also recorded, to be used as references.
* The diffraction intensity of a reflection of the drift correction disc material, , was also measured and recorded as a reference.

**Key**

|  |  |
| --- | --- |
| IRQz1 | intensity ratio “quartz (Qz1) to nickel(II) oxide (Bun1)” |
| W%RQz | percent weight ratio “quartz to nickel(II) oxide” |

**Figure D.3 — Calibration graph for primary reflection of quartz. Data in Table D.8 (from [8]).**

- The intensity ratios were plotted along the y-axis, and percent weight ratios of quartz to nickel(II) oxide along the x-axis of a calibration graph (Figure D.3 for ), and used to derive straight trend lines according to the method of least squares:

where

|  |  |  |
| --- | --- | --- |
|  |  | is the slope of the calibration line. No intercept appears in the equation, because the trend line was forced through zero. |

* + - 1. Determination of quartz in a sample

- A preliminary diffraction scan was carried out on a specimen of sample unmixed with any internal standard, for quartz identification (see Annex D.2.1.2). Line *Qz1* did not result affected by interferences, and was chosen to represent the sample in the quantitative analysis.

- A ~2 g mixture with 2/5 sample (*s*), 2/5 nickel(II) oxide (*Bun*) internal standard, and 1/5 of γ-aluminium(III) oxide (*diluent*) was prepared:

* 0,80042 g; 0,80002 g; 0,39988 g

- The specimen was analysed in the angular ranges of the primary peaks of quartz and bunsenite. The following intensities were measured:

* 16002 counts·°2θ
* 17321 counts·°2θ

- Calculation of the weight fraction of quartz in the sample, :

* 44,4
  1. Spiking method
     1. Determination of reference values

A diffraction analysis was performed on a pure quartz specimen (an automatic divergence slit was used in the incident beam). The following results for intensities and relative intensities were used as reference values for all the analyses performed by applying this method on unknown specimens:

* 53083 counts·°2θ 100
* 10588 counts·°2θ 20
* 5895 counts·°2θ 11
* 56%

The average values of *2θ*, *FWHM*, and *As* were also calculated for each diffraction line, and recorded as reference values.

* + 1. Determination of quartz in a sample
       1. Diffraction analysis on an undoped specimen – quartz identification

- A specimen from the undoped sample was prepared, and analysed for the three most intense diffraction lines of quartz.

- Quartz was identified, the following intensities were measured (the index *0* identifies data for undoped samples) and the relative intensities and ratio calculated:

* 634 counts·°2θ 100
* 107 counts·°2θ 17
* 50 counts·°2θ 8
* 47%

- Line *Qz1* did not appear affected by interference, and was chosen for quantification.

* + - 1. Estimation of the mass of quartz reference material to be added to the sample

- Estimation of approximate quartz percent weight fraction:

* 1,2

- The value of is below 20, therefore, the addition of a low concentration of dopant would negligibly change the mass absorption coefficient of the sample: the spiking method can be used.

- The specimen holders used for the analyses were tested, and contained 1,90-1,95 g of powder. Then, the aim was to prepare mixtures with a total weight of around 2,000 g. The additions of quartz reference material were planned to have the following mass values:

* Addition 1: 0,6 ; 0,012 g
* Addition 2: 1,2 ; 0,024 g
  + - 1. Preparation and analysis of two doped specimens

- Specimen with addition 1:

* Weighed materials: quartz 0,01070 g; sample 1,99122 g
* Effective addition 1: 0,53

- Specimen with addition 2:

* Weighed materials: quartz 0,02015 g; sample 1,98293 g
* Effective addition 2: 1,01

- After the analyses, the following diffraction intensities were measured:

* Specimen with addition 1: 761 counts·°2θ
* Specimen with addition 2: 864 counts·°2θ
  + - 1. Calibration line construction

- The graph “addition of vs. quartz line diffraction intensity” was constructed, and is represented in Figure D.4.

- Slope *a*=228,12, and intercept *b*=635,66, were calculated for the calibration line.

* + - 1. Calculation of the weight fraction of quartz in the specimen

The result of the analysis is:

2,7

**Key**

|  |  |
| --- | --- |
| IQz1 | quartz primary peak (Qz1) intensity (counts·°) |
| W%Qz.add | percent weight fraction of quartz addition |

**Figure D.4 — Calibration graph for primary reflection of quartz, where the diffraction intensity is a function of the quartz percent weight fraction addition.**

1. (informative)  
     
   Experimental procedure for the determination of LOD and LOQ
   1. Spiking method and internal standard method

A specimen of infinite thickness from a sample that produces an XRPD pattern not interfering with the quartz or cristobalite peak under examination is prepared according to the procedure described in Section 7. This specimen is used as a method blank for that specific diffraction peak of the analyte phase.

Note 1: Tables B.1 and B.2 in Annex B, for quartz and cristobalite respectively, can be used for choosing a suitable phase.

The specimen is mounted on the diffractometer and analysed by using the same instrument, instrumental setting, and acquisition programs used for the determination of the crystalline silica phase in unknown samples. The standard deviation σ of the intensity fluctuation in the angular range of the quartz or cristobalite peak of interest (blank measurement) is then calculated (Fig. E.1).

A number of blank measurements are carried out by using at least two different samples. The worst standard deviation result is used as a reference.

**Key**

|  |  |
| --- | --- |
| I | intensity (counts) |
| °2θ | diffraction angle |

**Figure E.1 — Example of a diffraction pattern for a specimen of pure rutile analysed in the angular range of the secondary peak of quartz (). Solid, dotted and dashed lines represent background, limit of detection and limit of quantification lines respectively. The calculated reference standard deviation σ is shown.**

The net height intensity that represents the limit of detection for the peak of the analyte , , is calculated as three times the reference standard deviation of the blank measurement. The net height intensity that represents the limit of quantification, , is calculated as ten times the reference standard deviation σ of the blank measurement (ISO 18158):

where and are expressed by using the same measurement unit (e.g. counts).

To determine the limit of quantification, a number of specimens should be prepared in the laboratory by mixing small known amounts (e.g. from 0.01% to 5%) of pure quartz (or cristobalite) with a sample which does not interfere with the quartz peak under examination.

Note 2: In the example shown in Figure E.2, a calcite sample was used to determine the LOQ of the secondary peak of quartz, Each specimen was analysed by using the same instrument, instrumental setting, and acquisition programs used in the laboratory for the determination of quartz in unknown samples.

A visual examination of the resulting diffraction patterns allows estimating an approximate value of (e.g. Fig. E.2). The net height intensity of each specimen is measured and a calibration graph, such as in Figure E.3, is constructed by using net height intensities and quartz (or cristobalite) content known from each experimental mixture. A straight-line calibration function can be used to calculate the limit of quantification for the weight fraction of the analyte by the analysis of peak :

where and are the intercept and slope of the calibration function. The line can generally be forced through the origin, so that =0.

**Key**

|  |  |
| --- | --- |
| I | intensity (counts) |
| °2θ | diffraction angle |

**Figure E.2 — Example of diffraction patterns for a calcite sample and specimens prepared from mixtures of calcite with pure quartz, analysed in the angular range of the secondary peak of quartz (). The known weight fractions of quartz are shown in the figure. Solid, dotted and dashed lines represent background, limit of detection and limit of quantification lines respectively. The reference standard deviation σ (from Fig. E.1) is shown.**

**Key**

|  |  |
| --- | --- |
| IH | net height intensity (counts) |
| W%Qz | quartz weight fraction (%) |

**Figure E.3 — Calibration line obtained from the data represented in Figure E.2. The slope of the straight line that passes through the origin and the calculations for and are shown.**

The value is used as a threshold value to assure quantitative measurement of an analyte accurately. Following a similar procedure, the , which represents a probability of 50 % that the analyte will not be detected when it is present at the concentration of the LOD, can be calculated.

Typical values for the limits of quantification of quartz and cristobalite obtained by the spiking method are:

- =0,1-0,2; =0,4-0,5; =0,6-0,7

- =0,2-0,3; =1-2 .

The limits of quantification of the internal standard method should be slightly worse compared with those obtained for the spiking method, since the silica peak intensities should result lower, due to the dilution of the sample with the internal standard material. For example, if a 30% weight fraction of internal standard material is added to a sample, the limits of quantification should result 30% higher than those presented above.

* 1. External standard method

The procedure described in E.1 can also be used when the sample is deposited on a filter and the external standard method is used for quantification. In this case, however, the limits of detection and quantification are calculated as weight (mass), and respectively.

The limits of detection and quantification expresses as weight fractions depend on the weight, , of sample deposited on the filter:

and

In fact, since the weight of sample should range between 1 and 5 mg (Section 7.7), the limits of detection and quantification can change from specimen to specimen, depending on the amount of powder deposited on the filter. Average limit values can be considered, according to the sample mass amount most often deposited in the laboratory.

The procedure for the assessment of the limits should include the preparation of a number of mixtures of low content (e.g. 0.2%-5%) of quartz (or cristobalite) with a sample not interfering with the crystalline silica diffraction peak of interest (see note in E.1). Amounts of 1-5 mg of powder from the mixtures and from the non-interfering sample are deposited on 25-mm diameter filters of the same type used in the laboratory for unknown samples (Section 7.7). Filters are then analysed according to the external standard method (Section 8.4.4).

The diffraction pattern obtained when only the non-interfering sample is deposited on the filter is used to calculate the standard deviation σ of the blank measurement. The result should look similar to that represented in Figure E.1.

The diffraction patterns from mixtures of quartz (or cristobalite) with a non-interfering sample should look similar to those represented in Figure E.2, and allow the construction of a calibration function similar to that shown in Figure E.3, finally leading to the calculation of the limits and for detection and quantification, respectively.

However, given the low amounts of powder deposited on filters, the preparation of homogeneous mixtures of very low known contents of crystalline silica within a mineral matrix is difficult. A simplified procedure, consisting in using the same calibration filters used for the construction of the calibration line (Section 8.4.4.2) is then allowed to assess the and limits. The resulting diffraction patterns should still appear similar to those represented in Figure E.2.

Typical values for the limits of quantification (weight fractions) of quartz and cristobalite obtained by the external standard method (3-4 mg of sample powder deposited on silver filters) are:

- =0,2-0,3; =0,8-1,2; =1-2

- =0,3-0,4; =3-3,5.

1. (informative)  
     
   Uncertainty of measurement

The analytical result from a single sample can vary by the analytical method and by the laboratory performing the analysis. A way to assess this variance is through inter-laboratory studies using well-described, homogenous samples. Members of the international standards working group for silica measurement that prepared this document collaborated to implement a small (six laboratories) inter-laboratory comparison study. The results from six laboratories for same measurand (quartz weight fraction) using the same method of analysis, and then by comparing the results for the three methods included in this document, were used to estimate the uncertainties of measurements.

Three powder mixtures with grain size in the optimal range for XRPD were prepared in a Reference Laboratory and sent to the other five laboratories involved in the testing. Each sample contained approximately 10% of in-house reference material of quartz (Sikron micronized flour SF800, SiO2 content = 97,5%, average grain size d50%=2 μm) thoroughly mixed with approximately 90% of a different pure mineral phase.

Sample no. 1 matrix was composed of pure barite, which produces a major interference with primary peak of quartz. Sample no. 2 matrix was composed of calcite, which should not interfere with the three most intense diffraction peaks of quartz. However, line Kβ of primary peak of calcite may produce a small interference on the primary peak of quartz, even though a monochromator is used for the measurement. Sample no. 3 matrix was composed of talc (Finntalc M15 – AW, 96% pure), which produces small interferences on both secondary and tertiary diffraction peaks of quartz.

Each participating laboratory prepared the specimens taking aliquots from the received powder samples without any further treatment except mixing, then carried out the XRPD analyses according to the three methods described in this document. Different quartz reference materials (NIST SRM 1878a, Quin1, A9950, Minusil-5, SF600 desludged, and an in-house reference material) were used in the laboratories for calibration line construction (external standard method), reference intensity ratio determination (internal standard method) and quartz addition (spiking method). Alumina powder (corundum) was generally used as the internal standard, but also anatase in one of the laboratories. Silver filter was the preferred collecting medium for depositing the sample according to the external standard method, but polycarbonate and pvc filters were used in two laboratories. Diffractometers were all equipped with copper X-ray tubes, except one where a cobalt tube was applied for the X-ray irradiation.

The assigned (consensus) value, in Table F.1, is calculated for each sample as weighted averaged result from all the measurements obtained for the same sample in the six laboratories by using the three analytical methods. The measurement uncertainty, , of the assigned value is assessed as:

where

is the uncertainty of the assigned values .

is the average between-laboratory standard deviation of participants results.

is the number of measurements performed on each sample.

**Table F.1 — Results of measurements and calculation of the assigned values**

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Method of analysis | y lab.1 | y lab.2 | y lab.3 | y lab.4 | y lab.5 | y lab.6 |  |  |  |  |
| **sample 1** | | | | | | | | | | |
| External standard | 9,8% | 8,8% | 10,1% | 8,3% |  | 10,5% | 15 | 10,4% | 1,8% | 0,46% |
| Internal standard | 9,9% | 10,6% | 11,6% | 10,1% | 11,9% | 11,7% |
| Spiking | 13,6% |  | 7,6% | 8,0% | 10,3% | **18,6%** |
| **sample 2** | | | | | | | | | | |
| External standard | 8,2% | 6,4% | 8,5% | 7,9% |  | 11,4% | 15 | 9,8% | 1,7% | 0,44% |
| Internal standard | 12,3% | **18,8%** | 9,0% | 9,4% | 10,0% | 10,4% |
| Spiking | 10,0% |  | 8,2% | 10,9% | 9,5% | 10,6% |
| **sample 3** | | | | | | | | | | |
| External standard | 10,1% | 7,4% | 10,3% | 8,9% |  | 13,8% | 16 | 9,7% | 1,6% | 0,41% |
| Internal standard | 11,6% | 8,8% | 8,3% | 9,5% | 9,5% | 9,8% |
| Spiking | 9,3% |  | 8,1% | 10,5% | 9,6% | 11,5% |
| **x,x%** : outlier; removal procedure: Grubbs test (2 tail, probability=2,5%) | | | | | | | | | | |

The measurement uncertainty of the method bias, , that characterizes the dispersion of the values that could reasonably be attributed to the measurand, includes the variation in laboratories’ result and the uncertainty of the assigned value (Table F.2):

where

is the mean standard deviation of measurements from assigned value .

**Table F.2 — Uncertainty estimation of the methods**

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| sample | y lab.1 | y lab.2 | y lab.3 | y lab.4 | y lab.5 | y lab.6 |  |  |  |  |  |  |
| **External standard method** | | | | | | | | | | | | |
| No. 1 | 9,8% | 8,8% | 10,1% | 8,3% |  | 10,5% | 8,9% | 1,2% | 10,0% | 1,9% | 0,43% | 2,0% |
| No. 2 | 8,2% | 6,4% | 8,5% | 7,9% |  | 11,4% | 8,2% | 1,9% |
| No. 3 | 10,1% | 7,4% | 10,3% | 8,9% |  | 13,8% | 9,9% | 2,4% |
| **Internal standard method** | | | | | | | | | | | | |
| No. 1 | 9,9% | 10,1% | 11,6% | 10,1% | 11,9% | 11,7% | 10,7% | 1,2% | 9,4% | 1,4% | 0,43% | 1,4% |
| No. 2 | 12,3% |  | 9,0% | 9,4% | 10,0% | 10,4% | 10,0% | 1,5% |
| No. 3 | 11,6% | 8,8% | 8,3% | 9,5% | 9,5% | 9,8% | 9,4% | 1,3% |
| **Spiking method** | | | | | | | | | | | | |
| No. 1 | 13,6% |  | 7,6% | 8,0% | 10,3% |  | 10,1% | 2,7% | 9,7% | 1,6% | 0,43% | 1,7% |
| No. 2 | 10,0% |  | 8,2% | 10,9% | 9,5% | 10,6% | 10,0% | 1,2% |
| No. 3 | 9,3% |  | 8,1% | 10,5% | 9,6% | 11,5% | 10,0% | 1,4% |

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