Annals of Work Exposures and Health, 2026, **70**, wxaf084
https://doi.org/10.1093/annweh/wxaf084
Advance access publication date: 18 December 2025
Original Article

Quantitative X-ray diffraction analysis of quartz in bulk samples: outcomes of an international interlaboratory test on three standardized methods

Marco Mecchia[1,*], Markus Mattenklott[2], Peter Stacey[3], Celine Eypert-Blaison[4], Emanuele Cauda[5], Gilles Mertens[6], Steve Clark[7], Frank Luetzenkirchen[8], Viola Schmidt[2], Rachel Walker[5], and Darren Musgrove[3]

[1]INAIL, Istituto Nazionale Assicurazione contro gli Infortuni sul Lavoro, Consulenza Tecnica per la Salute e la Sicurezza Centrale, via Roberto Ferruzzi 40, Roma 00143, Italy
[2]IFA, Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung, Alte Heerstraße 111, Sankt Augustin 53757, Germany
[3]HSE, Health and Safety Executive, Science and Research Centre, Harpur Hill, Buxton, Derbyshire SK17 9JN, United Kingdom
[4]INRS, Institut National de Recherche et de Sécurité, Centre de Lorraine, Département Métrologie des Polluants, Laboratoire d'Analyses Inorganiques et de Caractérisation des Aérosols, Rue du Morvan, CS 60027, Vandoeuvre Les Nancy Cedex 54519, France
[5]NIOSH, National Institute for Occupational Safety and Health, Center for Direct Reading and Sensor Technologies CDC, Pittsburgh, PA 15236, United States
[6]Qmineral bv, Gaston Geenslaan 1, Heverlee B-3001, Belgium
[7]IOM, Institute of Occupational Medicine, Research Avenue North, Riccarton, Edinburgh EH14 4AP, United Kingdom
[8]Quarzwerke GmbH, Service Department Law-Environment-Communication, Kaskadenweg 40, Frechen 50226, Germany

*Corresponding author: Email: marco.mecchia1@gmail.com

Abstract

The quantification of crystalline silica (quartz) in materials helps communicate the potential risk of exposure when the materials are then included in a work process that could generate an aerosol of particulate. Although many analytical laboratories have developed procedures for quantification of quartz in bulk samples, these procedures are not standardized and are generally limited to their individual needs. Therefore, the International Standards Organization (ISO) working group for silica measurement (ISO/TC146/SC2/WG7 Silica) developed an international standard that describes 3 analytical methods for the determination of quartz in bulk samples by X-ray diffraction (XRD): the external standard method for samples prepared on filters, the internal standard method, and the spiking method.

This paper describes the results of an interlaboratory measurement comparison in which the 3 XRD standardized methods were evaluated to verify if the 3 methods produce results that agree with each other. Simple analytical systems, represented by 4 binary mixtures of quartz added to another mineral, were prepared. Sub-samples of the 4 test powders were delivered to the 7 participating laboratories from 6 countries that agreed to participate in this study.

The precision of each measurement method, calculated as a percentage of quartz weight within the range 10 to 16 wt%, was similar for the 3 XRD methods. The repeatability SDs, s_r, ranged between 0.4 and 0.8 (relative SD, RSD_r, between 4.3% and 8.7%) for thin specimens on filter, 0.4 to 1.1 (RSD_r between 4.2% and 10.6%) for the internal standard method, and 0.3 to 1.2 (RSD_r between 3.7% and 11.9%) for the spiking method. The reproducibility SDs, s_R, of the results in the studied wt% range were between 1.1 and 2.1 (RSD_R between 12.7% and 21.5%) for the method of thin specimen on filter, 1.1 to 1.4 (RSD_R between 7.5% and 14.1%) for the internal standard method and 1.1 to 2.6 (RSD_R between 9.5% and 23.7%) for the spiking method. These methods obtained equivalent results at 2 concentration levels of 10% and 16% in these binary mixtures. A further step of interlaboratory testing should be implemented to investigate the performance of the 3 methods at the lower quartz concentration values.

Keywords: crystalline silica; laboratory comparison; round robin; standardized methods of analysis

Received: June 24, 2025, Accepted: November 9, 2025

What's Important About This Paper?

Knowledge of the proportion of crystalline silica in bulk materials used in workplaces is useful to help communicate the potential risk of exposure and inform risk assessments in many workplaces. This work reports an inter-laboratory study demonstrating the equivalence of 3 X-ray diffraction analysis methods to support their inclusion in a new international standard. The international standard provides new support for industry and institutional measurements of bulk samples from workplaces.

Introduction

Quartz is the most common form of silica and accounts for approximately 12% of the Earth's lithosphere (Clarke 1924). Excavating rocks, demolishing buildings, sawing, crushing, grinding, milling, or drilling of materials containing quartz, and the use of quartz-containing powders in manufacturing are work processes which generate quartz-containing dust. Exposure to quartz in the respirable fraction of inhaled dust is therefore a hazard to the health of workers in many industries. Identification of the source of exposure is a key factor in finding strategies for effectively reducing the risk. Consequently, the quantification of quartz content in rocks, bulk materials and products that have a potential risk of producing a significant respirable content when they are processed and become airborne in a workplace may help to communicate the potential risk of exposure for workers.

In the United States, all materials handled by OSHA-regulated facilities should be labelled according to the requirements of the Hazard Communication Standard and workers should receive proper training on the handling of the material if the crystalline silica content equals or exceeds 0.1%. In Europe, work involving exposure to respirable crystalline silica dust generated by a work process has recently been included in Annex I (list of substances, preparations, and processes) to Directive 2004/37/EC on the protection of workers from the risks related to exposure to carcinogens or mutagens at work.

Several X-ray powder diffraction methods are available for analyses of components in bulk materials and some of them have been specifically used for quantitative determination of quartz, such as the internal standard method (eg, Taylor 1978; Hardy 1992 ; Tomaino 1994 ; Blount and Carr 1994), the spiking (addition) method (eg Emig and Smith 1989; Renault et al. 1994; Salter and Riley 1994), the absorption diffraction method (eg Hurst 2012), the Rietveld pattern refinement (eg Jordan et al. 1990; Martin et al. 2012; Stacey 2019) and the external standard method for samples prepared on filters (eg Altree-Williams 1977; Salt 1985; Carter et al. 1987; NIOSH, 1994; Elton and Smith 1999; Radnoff and Kutz 2014; ISO 16258-2:2015).

It should be emphasized that although quartz is found as a minor or trace component in many materials in the workplace, it is generally the only analyte in these samples for which quantification is requested. While identification of quartz in a sample is rarely a problem (Elton and Smith 1999), standard procedures for the quantitative determination of quartz in bulk samples are difficult to certify because of the variability of the matrices and their potential interferences (Smith 1997). In fact, most bulk mineral powder and stone products, as well as atmospheric samples, usually contain mineral constituents with intensity peaks overlapping and interfering with some peaks of quartz in the diffraction analysis.

To help laboratories with routine analysis of quartz in bulk samples, the ISO working group for silica measurement (ISO/TC146/SC2/WG7 Silica) is developing an international standard for the measurement of quartz content in bulk samples by X-ray diffraction (XRD) which includes 3 common analysis procedures: an external standard method for samples prepared on filters, an internal standard method, and a spiking method.

To improve the understanding of these standardized measurement methods for routine analysis, the ISO working group on silica organized a laboratory comparison in which the 3 methods were tested to verify if they produced results that agree with each other. In this comparability study, the aim was to assess the accuracy and precision expected in samples at levels between 10% and 16% weight quartz. Seven laboratories from 6 different countries, members of the WG7, agreed to participate in an international laboratory comparison for the XRD analysis of 4 artificial powder samples were prepared from binary mixtures of 2 components ie quartz and another mineral. It should be highlighted that determining quartz in a sample consisting of a binary mixture of minerals is generally easier than in a multi-phase sample with many crystalline components. In addition, the difficulty of preparing artificial samples with a known and controlled analyte content increases as the number of added minerals increases.

Therefore, this laboratory comparison demonstrated the comparability of these methods and estimated repeatability and reproducibility SDs in the specific conditions investigated, which included interferent minerals with complex diffraction patterns with a range of absorption coefficients.

The international standard ISO 5725-2 (2019) provides a basic method for their determination; however, it was not possible to completely fulfil the requirements of this ISO standard. The limitations of this laboratory

comparison to comply fully with ISO 5725-2 are described in the following sections. Therefore, the results reported in this paper should be considered as a first contribution to the development of a more comprehensive assessment of the accuracy of the measurement methods. Further investigations into the capability of these methods to quantify crystalline silica in bulk samples at sufficiently low levels are also considered necessary before they can be confidently utilized to quantify crystalline silica in samples at regulatory levels (eg 0.1% or 1%) adopted in some countries.

Diffraction analysis methods

Three quantitative powder X-ray diffraction standardized methods (ISO 6868 draft standard) were tested:

(i) "External standard method" for thin specimens deposited on filters.
(ii) "Internal standard method" for specimens with infinite thickness.
(iii) "Spiking method" for specimens with infinite thickness.

External standard method—thin specimen on filter

The external standard method was applied by measuring the diffraction intensity of a quartz reflection j in a specimen of the sample (containing an unknown concentration of quartz). This diffraction intensity was then compared with a calibration curve of "quartz weight versus intensity" constructed from specimens with known (weighed) amounts of quartz. This external standard method was applied to thin specimens obtained by depositing small amounts (1 to 5 mg) of sample on 25-mm filters. For this purpose, the powdered sample was placed in a beaker, 2-propanol was added and the beaker was placed in an ultrasonic bath. After sonication, the suspension was poured into a filtration apparatus and the powder was collected on the surface of a membrane filter. The amount of sample was calculated by weighing the filter on a microbalance before and after the deposition. The filter was then placed on a metallic (eg, aluminium or zinc) support disc and mounted in an appropriate specimen holder for the diffraction analysis.

The calibration curve was constructed by analysing several calibration filters prepared by depositing known amounts (range ≈0.01 to 5 mg) of powdered quartz reference material (RM). Quartz reference materials are usually not completely crystalline, due to a thin layer of disordered (amorphous silica) structure on the surface of each particle of approximately 0.03 µm thick (Gordon and Harris 1955). Therefore, it was necessary to correct the weight of quartz deposited on the calibration filters by considering the 'crystallinity' X_{RM} of the reference material (Table 1).

This method also required the correction of the effects of X-ray absorption and for the variation with time of the intensity of the incident X-ray beam.

When a very thin layer of powder is deposited on a filter, the diffraction intensities from all the phase reflections in a specimen are linear functions of the irradiated weight of each phase. However, if the mass deposited on the filter (1 to 5 mg) is not thin enough, then X-ray radiation is partially absorbed by the specimen itself and the measured value is less accurate. The measured intensity deviates from the theoretically linear intensity resulting in lower reported results. Therefore, a correction factor $f_{ab,j}$, specific for each peak j and which depends on the specimen absorption characteristics, should be calculated. The procedure for absorption correction is reported in the supplementary materials.

A correction factor f_{em} for the drift in X-ray radiation intensity from the day of instrument calibration was also applied for comparing the diffraction result on the specimen with that from the calibration curve (see supplementary materials).

The corrected diffraction intensity of a quartz peak j was calculated as:

$$I_{Qzj,C} = f_{ab,j} \cdot f_{em} \cdot I_{Qzj} \quad (1)$$

The calibration function for a quartz peak j was calculated from quartz weight wt and $I_{Qzj,C}$ measured on calibration filters. A straight trend line, according to the method of least squares, was used:

$$I_{Qzj,C} = a_j \cdot wt + b_j \quad (2)$$

where a_j and b_j are the slope and the intercept of the line. The calibration slope and intercept were used to determine the quartz weight wt in a specimen from the value $I_{Qzj,C}$ measured in the specimen:

$$wt = \frac{I_{Qzj,c} - b_j}{a_j} \quad (3)$$

The quartz percent weight fraction was finally calculated as:

$$wt\% = wt \cdot 100/wt_{spc} \quad (4)$$

where wt_{spc} is the known weight of the specimen.

Internal standard method—infinite thickness specimen

Infinitely thick (>0.3 mm) specimens were prepared from mixtures of quartz RM with an Internal Standard (IS) from a mineral phase that was not present in the samples, and the responses from diffraction analyses were used to calculate intensity ratios. This method

Table 1. Diffraction systems, reference materials, and filters used for deposition of the laboratories participant in the interlaboratory tests.

	Laboratory						
	1	*2*	*3*	*4*	*5*	*6*	*7*
Diffractometer	Panalytical X'Pert Pro MPD	Panalytical Empyrean	Bruker D8 Advance	Panalytical X'Pert Pro MPD	Panalytical X'Pert Pro MPD	Panalytical Empyrean	Bruker D2 Phaser
X-ray radiation source	Copper	Copper	Copper	Copper	Copper	Cobalt	Copper
(power level—kV;mA)	(40;40)	(45;40)	(40;40)	(50;45)	(45;40)	(40:40)	(30:10)
Divergence slit	Automatic	Automatic	Automatic	Automatic	Fixed	Fixed	Fixed
Monochromator	Yes	Yes	No	No	No	Yes	No
Ni filter	No	No	No	Yes	No	No	Yes
Detector	Pixcel 1-D	Pixcel 3-D mode 1-D	LynxEye XE-T	Pixcel 1-D	Pixcel and Xcelerator	Pixcel 1-D	LynxEye 1-D
Quartz refer. material (crystallinity %)	NIST1878a[a] (93.7) In-house[b,c] (100.0[e])	NIST1878a[a,b] (93.7)	A9950[a] (89.3) In-house[b,c] (100.0[e])	NIST1878a[a,c] (93.7) A9950[b] (89.3)	Minusil-5[b,c] (95.0[e])	SF600[a,b,c] (96.0[d])	A9950[a,b] (89.3)
Internal Standard Material[b]	Corundum (Al_2O_3)	Corundum (Al_2O_3)	Corundum (Al_2O_3)	Bunsenite (NiO)	Corundum (Al_2O_3)	Corundum (Al_2O_3) Anatase (TiO_2)	Corundum (Al_2O_3)
Deposition filter[a] (diameter—mm) (porosity—µm)	Silver (25) (0.45)	Polycarbon. (25) (0.4)	PVC (25) (5)	Silver (25) (0.45)	—	Silver (25) (0.2)	PVC (25) (5)

[a]External Standard Method on filter. [b]Internal Standard Method. [c]Spiking Method. [d]Purity of the reference material determined by phase contrast microscopy; crystallinity is not known. [e]Crystallinity of the reference material assumed by the participant.

is most often applied following the reference intensity ratio (RIR) approach, in which a fixed weight percent fraction (eg, $wt\%_{IS}$:$wt\%$ ≈ 50:50) is used. The crystallinity value of the quartz reference material, X_{RM}, can be used to correct the weight percent of quartz.

Diffraction analyses were carried out to determine the intensity I_{Qzj} of a reflection j of the quartz RM, and the intensity I_{ISk} from a reflection k of the IS phase. The intensity ratio $IR_{Qzj/ISk}$ for each combination of quartz and IS peaks was calculated as:

$$IR_{Qzj/ISk} = \frac{I_{Qzj}}{I_{ISk}} \cdot \frac{wt\%_{IS}}{wt\%} \tag{5}$$

The average value for $IR_{Qzj/ISk}$ from several tests carried out in the laboratory was used as the reference intensity ratio $RIR_{Qzj/ISk}$.

To determine the quartz content in a sample containing an unknown quartz concentration, a specimen was prepared from a mixture of the sample and internal standard in known proportions. Diffraction analyses were performed to measure the intensity of a peak from the IS and the most intense peak of quartz not affected by interference. The intensity ratio $IR_{Qzj/ISk}$ in the specimen was then calculated and compared with the $RIR_{Qzj/ISk}$ determined in the same laboratory:

$$wt\% = \frac{I_{Qzj}}{I_{ISk}} \cdot \frac{wt\%_{IS}}{100 - wt\%_{IS}} \cdot \frac{100}{RIR_{Qzj/ISk}} \tag{6}$$

In this method, it was not necessary to consider the X-ray absorption factor, which is eliminated by the equation. In fact, the variation of absorption due to the variation of the relative amounts of the other phases present in the mixture should not significantly affect the ratio between the diffraction intensities of quartz and internal standard since such variations equivalently affects both the intensities. Also, the change with time of the X-ray radiation intensity emitted from the X-ray tube does not influence the reported result.

A variation of the RIR approach consisted in the construction of a calibration line for the variation of the ratio I_{Qzj}/I_{ISk} in specimens prepared with the ratio $wt\%_{IS}/wt\%$ distributed over the entire range of possible values. Following the procedure recommended by Taylor (1978), a diluent/grinding amorphous phase was also added to the mixture (eg sample:internal standard:diluent = 1:1:1).

Spiking method—infinite thickness specimen

Infinitely thick specimens were prepared from the pure sample and from at least 2 mixtures of the sample with the addition of appropriate weight fractions (eg, approximately the expected quartz content and half that value) of a quartz RM. The crystallinity value of the quartz reference material, X_{RM}, used in the preparation of the mixture should be applied to correct the weight fractions of quartz.

The method assumes that the additions of quartz RM dopant to the sample cause negligible changes in its mass absorption coefficient. In practice, this assumption is valid if the addition of quartz dopant is relatively small (eg, $wt\%_{add} < 20$) or when the mass absorption coefficient of the sample matrix is known to be close to that of quartz.

The percent weight of quartz in the sample, $wt\%$, was determined through a calibration line constructed for each individual sample by plotting the diffraction intensity results for a quartz peak j ($I_{Qzj,add0}$, $I_{Qzj,add1}$ and $I_{Qzj,add2}$) vs. the quartz percent weight added to the sample ($wt\%_{add0} = 0$, $wt\%_{add1}$ and $wt\%_{add2}$). The diffraction intensity of the peak should be a linear function of the dopant:

$$I_{Qzj,add} = a_{j,add} \cdot wt\%_{add} + b_{j,add} \tag{7}$$

where $a_{j,add}$ and $b_{j,add}$ are the slope and intercept of the line. The percent weight fraction of quartz in the unknown sample was:

$$wt\% = \frac{b_{j,add}}{a_{j,add}} \cdot \left(1 - \frac{b_{j,add}}{a_{j,add} \cdot 100}\right) \tag{8}$$

Experimental

Samples

Four well mixed binary mixtures of powders in known proportions and grain size in the optimum range for XRD analysis were prepared using highly crystalline phases. The optimum size of particles in a specimen for an XRD analysis is in the range 1 to 10 μm and preferably smaller than 5 μm (Klug and Alexander 1974). Grain size distribution in a powder sample can be verified, for instance, by laser scattering, and represented by its equivalent mean diameter (D_{50}).

Three mixtures of 10% by weight Sikron SF800 commercial micronized quartz flour and a different phase were prepared in the Institut für Arbeitsschutz der Deutschen Gesetzlichen Unfallversicherung (IFA) laboratory in Germany. Baryte ($BaSO_4$), calcite ($CaCO_3$), and talc ($Mg_3Si_4O_{10}(OH)_2$) were selected as matrix components. The baryte comes from a natural deposit. The finely ground material was sold as a product labelled C11. The calcite used is a very fine-grained product, so-called chalk (Type: Omega BLP 3). XRD analyses show a small portion of TiO_2. Both materials have a grain size distribution with a substantial proportion of respirable-sized particles. A commercial product, Finntalc M15, was used as talc phase; according to the manufacturer, the material is ≈96% pure talc with a median particle size $D_{50} = 5$ μm.

A fourth binary mixture was prepared at Health and Safety Executive (HSE) laboratory in the United Kingdom, by mixing 15.8% by weight of A9950 quartz respirable reference material in anorthite ($CaAl_2Si_2O_8$) powder British Chemical Standard (BCS)—Certified Reference Material (CRM) 529 Anorthic Feldspar. The particle diameter range was determined using laser diffraction (Particle Technology Ltd, Derby, United Kingdom). The volume median particle diameter for anorthic feldspar BCS-CRM 529 was 5.45 μm with a 90th percentile of 8.9 μm.

In all the 4 samples, at least 1 of the 3 most intense peaks of quartz was free from interference or showed little peak overlap (see supplementary materials, Fig. S1). The minerals in the mixtures exhibited a significant amount of absorption contrast; the calculated mass absorption coefficients (Cu) were: $\mu_{talc} = 26.34\ cm^2\ g^{-1}$, $\mu_{quartz} = 34.45\ cm^2\ g^{-1}$, $\mu_{anorthite} = 50.29\ cm^2\ g^{-1}$, $\mu_{calcite} = 70.94\ cm^2\ g^{-1}$, $\mu_{baryte} = 209.57\ cm^2\ g^{-1}$.

Subsamples of the 4 test powders (bottles with approximately 10 g each) were dispatched to the laboratories involved in the round robin. Although different sample portions were used for analysis in different laboratories, the materials were sufficiently homogenized before preparing the samples for dispatch to ensure that they could be presumed to be identical for practical purposes.

The homogenization of the 3 mixtures prepared at the IFA laboratory was achieved by the procedure that follows. First, 15 g of quartz and 15 g of the accompanying substance were placed in a plastic sample container. After adding 2 steel balls, a mixer mill (laboratory ball mill) was operated at 10 Hz for 10 min for an initial homogenization of the powders. Then, another 120 g of the accompanying substance was added to achieve a quartz content of 10% by mass, and the mixture was homogenized again in the mixer mill. After a subsequent manual mixing process for 5 min (tilting and rolling the container), the mixture was homogenized again with the mill.

The powder of the fourth mixture was prepared at the HSE laboratory by mixing in a figure of 8 mill for 4 hours. Subsamples from the top, middle, and bottom of the sample were measured before bottling. Scans were collected from each sample sent to the laboratories. Five analysts at HSE measured quartz in a random selection of samples before dispatch using the in-house method based on the internal standard method, which achieved a SD of 0.51.

Quartz reference materials (RMs)

Quartz RMs used by the participant laboratories

All 3 X-ray diffraction methods of quantification discussed in this paper require a calibration, which involves the use of a quartz RM. This RM is used for the preparation of calibration filters in the external standard method, for preparation of IS-quartz mixtures used for RIR calculation in the internal standard method, and for additions to the sample when the spiking method is applied. As can be seen in Table 1, different quartz RM were sometimes used in the same laboratory when different methods were applied.

Several quartz RMs are commercially available, and an RM can also be prepared in the laboratory. Any quartz RM should be characterized for particle size distribution and for purity/crystallinity. In fact, reliable results from an XRD analysis are obtained when the RM used for the specimen preparation has a grain size close to that of the samples. It is also clear that using quartz RMs with different crystallinities for calibration purposes will lead to different results. Therefore, diffraction responses (or alternatively quartz weights) should be corrected considering the crystallinity of quartz RM. The quartz RMs commercialized by the National Institute of Standards and Technology (NIST) are certified for quartz crystallinity, ie, the Standard Reference Materials SRM 1878a (X_{SRMa}=93.7% ± 0.21% quartz; $D_{50} = 1.59$ μm—NIST 2005) and SRM 1878b (X_{SRMb}=96.73% ± 0.40% quartz; $D_{50} = 3.33$ μm—NIST 2017), where uncertainties of crystallinity are expressed as a 95% confidence interval in the absence of systematic error. Crystallinity of quartz reference material A9950 is certified as 89.3% ± 3.6% (2σ) by comparison to the NIST SRM 1878a (HSE 2022). According to ISO 24095, following the work by Kauffer et al. (2002) and Stacey et al. (2009), the crystallinity of a quartz RM (X_{RM}) can be determined by comparing the average diffraction intensity of quartz primary peak ($\bar{I}_{Qz1,RM}$) from a number of specimens prepared with the quartz RM deposited on filters with that measured on specimens with equal masses of NIST SRM 1878a ($\bar{I}_{Qz1,SRMa}$):

$$X_{RM} = X_{SRM} \cdot \frac{\bar{I}_{Qz1,RM}}{\bar{I}_{Qz1,SRMa}} \quad (9)$$

Stacey et al. (2009) experimentally determined the crystallinity of several quartz RMs. Table 1 shows the quartz RMs used in the round robin with their crystallinity assigned by laboratories and applied to correct the value of quartz mass in the preparation of specimens. Two in-house reference materials with grain sizes larger than NIST SRMs were determined to be 100% quartz by the participants, using the experimental procedure described in Stacey et al. (2009). Larger particle-sized dusts could have smaller amorphous proportions and provide higher XRD intensities (larger range of crystalline zones) than that of the NIST standards which are respirable-sized.

Quartz RMs used for the preparation of the binary mixtures of powders

Sikron SF800 commercial micronized quartz flour (Quarzwerke—Frechen, Germany) was used at IFA

for the preparation of mixtures. According to its manufacturer, the SiO_2 content is ≈97.5%, with Al_2O_3 being the major contamination (≈2%), and its average grain size is 2 µm. A9950 quartz respirable reference material, produced by HSE via a cyclonic sedimentation process from Quarzwerke Sikron F600, was used at HSE for the preparation of the fourth sample. According to Stacey et al. (2009), the A9950 quartz powder has a crystallinity of 89.3%.

XRD measurements

All the participants performed the analyses using Bragg-Brentano X-ray diffraction instrument geometries. The measurement conditions are summarized in Table 1.

Silver, polycarbonate, and PVC filters were used as collection substrates (Table 1). The pore size of the filter does not dictate the particle size collected. There are several mechanisms by which particles are collected onto filter surfaces. Impaction is one mechanism where particles accumulate, due to the moment of inertia, through a complex path of filter fibres. Pore sizes also get smaller as particles accumulate and they become more efficient at collecting smaller particulate. Liu et al. (1983) states that PVC filters are 96.7% to 99.99% efficient for the collection of nanosized aerosol particulate, whilst 0.45 µm pore size silver filters are 93.6% to 99.9% for particles less than 1 µm.

The 3 most intense peaks of quartz, Qz1 [101], Qz2 [100], and Qz3 [112] were generally measured by all the laboratories. Each laboratory applied its own software and computational procedure that it routinely uses to measure the net area intensity of peaks. However, intensity net height was used in Lab. 4 for the spiking method.

The result for the primary peak, Qz1, was reported unless an interference affected its intensity, in which case peak Qz2 or Qz3 was chosen. One of the laboratories calculated the average result from the 3 peaks whenever possible. Details of specimen analysis, such as the instrument conditions, were left to the discretion of the participant.

The external standard method was carried out by analysing up to 3 specimens deposited on filters; the test result was calculated as the arithmetic mean of their individual results.

All laboratories obtained a single test result for each sample, except Lab. 1, which deposited 6 specimens on filters from each sample and analysed them under repeatability conditions to obtain a total of 3 test results for each sample.

For the preparation of infinitely thick specimens, all laboratories followed the standard technique of back packing to fill the cavity of the powder mount. Although this preparation technique subjects the particles to some crystallographic preferred orientation, experimental evidence showed good measurement of repeatability when quartz is the analyte.

The internal standard method was applied by analysing a single specimen following the RIR approach and using corundum (Al_2O_3) as the IS phase, but Lab. 6 also used anatase (TiO_2) as an internal standard material. Lab. 4 followed the calibration graph approach, in place of the RIR. In this case, bunsenite (NiO) was used as the IS phase, and gamma aluminium oxide Al_2O_3 powder was added to the mixture as diluent/grinding agent.

Analyses for the spiking method were carried out on 3 specimens: without quartz addition and 2 specimens with increasing additions.

A single test result for each specimen was provided by all the laboratories to test both internal standard and spiking methods, except Lab. 1, where new specimens were prepared to replicate the test under repeatability conditions, and a total of 3 independent test results were obtained with the same method on the same sample.

Some laboratories did not take part in the complete experiment (see results in Table 2).

Statistical methods

Precision experiments

The data 'not marred by method deviations, instrument malfunctions, unexpected occurrences during performance, or by clerical, typographical and arithmetical errors' (Horwitz 1995) from all the laboratories were used as the set of valid data. The Grubbs' test (2 tail, at a significance level $\alpha = 0.05$) outlier removal procedure was applied to test results obtained from all quartz percent weight measurements, after verification that the data were approximately normally distributed. The identified outliers were removed from the data set.

The general mean $\overline{\overline{wt\%}}_i$ (or grand mean, ISO 5725-1) for sample i analysed by a measurement method m, is calculated from all the test results obtained by all the laboratories, after eliminating outliers. Details on its calculation are given in the supplementary material.

The precision, the closeness of agreement between test results of a method, is expressed in terms of 2 conditions: the estimate of repeatability SD (s_r) and the estimate of reproducibility SD (s_R). In repeatability conditions, independent measurement results are obtained with the same analytical method on identical test powders in the same laboratory by the same operator using the same equipment within a short interval of time. In reproducibility conditions, independent measurement results are obtained with the same analytical method on identical test powders in different laboratories, with different operators using different equipment.

Table 2. Quartz percent weight (*wt*%) in bulk samples analysed by the 3 methods.

Laboratory no.	Sample 1 quartz-baryte Test results		Sample 2 quartz-calcite Test results		Sample 3 quartz-talc Test results		Sample 4 quartz-anorthite Test results	
	Method for thin specimen on filter							
1	10.3	(11.9; 8.7)	8.2	(8.0; 8.5)	10.1	(9.3; 10.9)	17.4	(17.8; 17.1)
	8.8	(7.8; 9.8)	9.1	(9.2; 9.0)	9.5	(9.2; 9.9)	16.3	(15.9; 16.8)
	9.1	(8.7;9.5)	9.5	(9.3; 9.7)	9.3	(9.5; 9.1)	16.2	(16.6; 15.8)
2	8.8	(9.2; 9.8; 7.4)	6.4	(6.4; 6.3; 6.4)	7.4	(7.5; 7.4; 7.4)	13.1	(12.6; 13.1; 13.5)
3	7.4	(7.4)	7.1	(7.1)	9.4	(9.4)	—	
4	8.1	(7.7; 8.2; 8.5)	7.8	(7.8; 7.9; 7.6)	9.0	(8.8; 9.1; 9.1)	18.0	(18.4; 18.0; 17.6)
6	10.5	(10.5)	11.4	(11.4)	13.8	(13.8)	16.3	(16.3)
7	—		—		—		13.1	(15.0; 13.0; 11.2)
	Internal standard method							
1	11.6		12.3		11.6		16.7	
	10.0		10.2		10.7		15.8	
	9.9		10.8		11.2		15.4	
2	10.1		17.9[a]		8.4		13.1	
3	11.6		9.0		8.3		—	
4	9.0		8.4		8.5		15.8	
5	11.9		10.0		9.5		16.7	
6	11.7		10.4		9.8		16.0	
7	—		—		—		16.0	
	Spiking method							
1	13.6		10.0		9.4		17.6	
	11.8		9.3		10.3		16.0	
	12.4		9.5		8.0		15.3	
3	7.6		8.2		8.1		—	
4	8.5		11.5		11.1		16.5	
5	10.8		9.9		10.0		16.0	
6	18.6[a]		10.6		11.5		19.5	

[a]Outlier, discarded from data set. The test results of the method for thin specimen on filter were derived from the observed values in parentheses.

The repeatability variance for analyses on a sample i is given by

$$s_{r,i}^2 = \frac{\sum_{l=1}^{n_l} (n_{l,i} - 1) \cdot s_{l,i}^2}{\sum_{l=1}^{n_l} (n_{l,i} - 1)} \quad (10)$$

where n_l is the number of laboratories in which repeatability was determined, and $s_{l,i}$ is the estimate of SD from test results for sample i obtained in a laboratory.

In this preliminary study, however, repeatability was determined in only one laboratory where 3 test results $wt\%_{l,it}$ were obtained for each sample by each method. A test result corresponds to a single observed value in the case of internal standard and spiking methods, while a test result from the method for thin specimen on filter is calculated as the arithmetic mean of analyses on 2 different filters. Therefore, in this case $s_{r,i}^2 = s_{l,i}^2$. Then based on these results from one laboratory, it was assumed that all laboratories had the same repeatability $s_{r,i}^2$.

The reproducibility variance is the sum of repeatability and between-laboratory variances:

$$s_{R,i}^2 = s_{r,i}^2 + s_{L,i}^2 \quad (11)$$

The between-laboratory variance ($s_{L,i}^2$) is a measure for variation between all the participating laboratories, and the procedure for its calculation is provided in the supplementary material. Both $s_{r,i}^2$ and $s_{L,i}^2$ are positive values, therefore repeatability describes the minimum variability expected from an analysis, while reproducibility is the maximum variability in results.

Repeatability and reproducibility relative SDs, RSD_r and RSD_R respectively, can be calculated as the SD divided by the general mean, expressed as a percentage.

The dependence of the variance upon $\overline{wt\%_i}$ was not thoroughly investigated in this study. In fact, 3 out of the 4 samples were prepared with approximately the same quartz percent weight value of 10.0, while the fourth sample was prepared with wt% ≈ 15.8.

Therefore, only a small range of $\overline{\overline{wt\%}}_i$ values was investigated.

Although the 4 binary mixtures of quartz and a second mineral were prepared according to a specific ratio, the experimental procedure for making the mixtures cannot guarantee full compliance with the expected proportions. For this reason, the accepted reference quartz percent weight value $wt\%_{\mathrm{ref},i}$ of each sample i, was the mean of the set of measurement results obtained from all the laboratories, and from all the methods m. A weighting factor (Mandel 1964) was defined for each method at a quartz percent level y, and used to correct for the different number of samples analysed by each laboratory (see supplementary material).

In this study, for each method, we consider 2 levels, a lower level $y1$ for samples no. 1, 2, and 3, with quartz percent weight $\overline{\overline{wt\%}}_{y1}$ and reproducibility variance $s^2_{R,y1}$, and an upper level $y2$ for sample no. 4 with $\overline{\overline{wt\%}}_{y2}$ and $s^2_{R,y2}$ (see material).

The estimate of the bias of a measurement method at a level y is given by the difference between the grand mean of test results from all the laboratories at that level and the accepted reference value $wt\%_{\mathrm{ref},y}$:

$$\delta_{m,y} = \overline{\overline{wt\%}}_y - wt\%_{\mathrm{ref},y} \tag{12}$$

where the reference value of the lower level $wt\%_{\mathrm{ref},y1}$ is calculated as the average of $wt\%_{\mathrm{ref},i1}$, $wt\%_{\mathrm{ref},i2}$ and $wt\%_{\mathrm{ref},i3}$, and the reference value of the upper level is $wt\%_{\mathrm{ref},y2} = wt\%_{\mathrm{ref},i4}$. The bias estimate can be positive or negative, and different at different levels y (ISO 5725-4).

According to ISO 5725-4, an approximate 95% CI for the estimate of the bias of the measurement method can be calculated as

$$\delta_{m,y} - A \cdot s_{R,m,y} \le \delta_{m,y} \le \delta_{m,y} + A \cdot s_{R,m,y} \tag{13}$$

where $s_{R,m,y}$ is the reproducibility SD of test results obtained for method m at level y, and A is a factor used to calculate the uncertainty of an estimate (for further details, see supplementary material).

Comparison of measurement methods

The results of the precision experiments described above were also used to verify the equivalence of the 3 methods, for the quartz percent level $y1$ at which the number of samples analysed by each laboratory was $n_{s,m} = 3$ for all the methods. Comparisons were conducted between pairs of alternative methods $m = 1$ and 2, $m = 1$ and 3, and $m = 2$ and 3 by using (ISO 5725-6):

(i) a two-tailed F-test with level of significance $\alpha = 0.05$, to check whether the variances of the 2 methods were equal;

(ii) the difference between the grand means $\overline{\overline{wt\%}}_{m,y}$ of the 2 methods, to check whether they were statistically insignificant.

Comparison of precision

The within-laboratory precision test statistic F_r for the comparison between alternative methods $m = 1$ and $m = 2$ at a quartz percent level y, is calculated as follows:

$$F_r = \frac{s^2_{r,m=2}}{s^2_{r,m=1}} \tag{14}$$

where the larger variance is always the numerator and the smaller the denominator.

The hypothesis of equal variances is rejected if F_r is greater than an upper critical value $F_{\alpha/2(v_{r,m=2},v_{r,m=1})}$ or less than a lower critical value $F_{(1-\alpha/2)(v_{r,m=2},v_{r,m=1})}$, and $v_{r,m=1}$ and $v_{r,m=2}$ are the associated numbers of degrees of freedom (for further details, see supplementary material).

The overall precision test statistic F_R is given by:

$$F_R = \frac{s^2_{R,m=2} - (1 - 1/n_{s,m}) \cdot s^2_{r,m=2}}{s^2_{R,m=1} - (1 - 1/n_{s,m}) \cdot s^2_{r,m=1}} \tag{15}$$

The hypothesis of equal variances is rejected if F_R is greater than an upper critical value $F_{\alpha/2(v_{R,m=2},v_{R,m=1})}$ or less than a lower critical value $F_{(1-\alpha/2)(v_{R,m=2},v_{R,m=1})}$ (see supplementary material).

Comparison between the means of methods

The difference between the grand means $\overline{\overline{wt\%}}_{m,y}$ of the test results of 2 methods $m = 1$ and $m = 2$ tested in all the laboratories at a quartz percent level y is statistically insignificant if:

$$\left| \frac{\overline{\overline{wt\%}}_{m=1,y} - \overline{\overline{wt\%}}_{m=2,y}}{\sqrt{s^2_{m=1} + s^2_{m=2}}} \right| \le 2.0 \tag{16}$$

where

$$s^2_{m=1} = [s^2_{R,m=1} - (1 - 1/n_{s,m}) \cdot s^2_{r,m=1}]/n_{l,r,m=1} \tag{17}$$

$$s^2_{m=2} = [s^2_{R,m=2} - (1 - 1/n_{s,m}) \cdot s^2_{r,m=2}]/n_{l,r,m=2} \tag{18}$$

where $n_{l,r,m=1}$ and $n_{l,r,m=2}$ are the numbers of laboratories participating in the repeatability experiments for methods 1 and 2 at quartz percent level y.

Results

The results for each sample and method from all participants to the interlaboratory comparison are given in Table 2. Not all the laboratories carried out the

Table 3. Estimation of repeatability and reproducibility SDs and bias of the measurement methods.

	Method for specimen on filter	Internal standard method	Spiking method		Method for specimen on filter	Internal standard method	Spiking method
Repeatability SD				Estimate of bias of the measurement method			
$s_{r,i1}$	0.79	0.95	0.92	δ_{i1}	−1.11	0.60	0.66
$s_{r,i2}$	0.64	1.08	0.36	δ_{i2}	−0.95	0.71	0.41
$s_{r,i3}$	0.40	0.45	1.16	δ_{i3}	0.02	−0.02	0.00
$s_{r,y1}$	0.61	0.83	0.81	δ_{y1}	−0.68	0.43	0.36
$s_{r,i4} = s_{r,y2}$	0.68	0.67	1.18	$\delta_{i4} = \delta_{y2}$	−0.41	−0.59	0.86
Reproducibility SD				$A \cdot s_R$			
$s_{R,i1}$	1.14	1.11	2.55	$A \cdot s_{R,i1}$	0.93	0.81	2.45
$s_{R,i2}$	1.79	1.29	1.11	$A \cdot s_{R,i2}$	1.54	1.01	0.96
$s_{R,i3}$	2.10	1.38	1.39	$A \cdot s_{R,i3}$	1.83	1.09	1.10
$s_{R,y1}$	1.68	1.26	1.69	$A \cdot s_{R,y1}$	1.44	0.97	1.50
$s_{R,i4} = s_{R,y2}$	2.02	1.20	1.80	$A \cdot s_{R,i4} = A \cdot s_{R,y2}$	1.74	1.01	1.85
Grand mean of test results in all the laboratories				Approximate 95% CI for the estimate of the bias			
$\overline{\overline{wt\%}}_{i1}$	9.01	10.73	10.78	Level $y1 = 9.8$	7.7 to 10.5	9.2 to 11.2	8.6 to 11.6
$\overline{\overline{wt\%}}_{i2}$	8.49	10.16	9.86	Level $y2 = 16.1$	14.0 to 17.5	14.5 to 16.5	15.1 to 18.8
$\overline{\overline{wt\%}}_{i3}$	9.79	9.75	9.77	Accepted reference values			
$\overline{\overline{wt\%}}_{y1}$	9.10	10.21	10.14	$wt\%_{\text{ref},i1}$	$wt\%_{\text{ref},i2}$	$wt\%_{\text{ref},i3}$	$wt\%_{\text{ref},i4}$
$\overline{\overline{wt\%}}_{i1i4} = \overline{\overline{wt\%}}_{i1y2}$	15.71	15.54	16.98	10.1	9.4	9.8	16.1

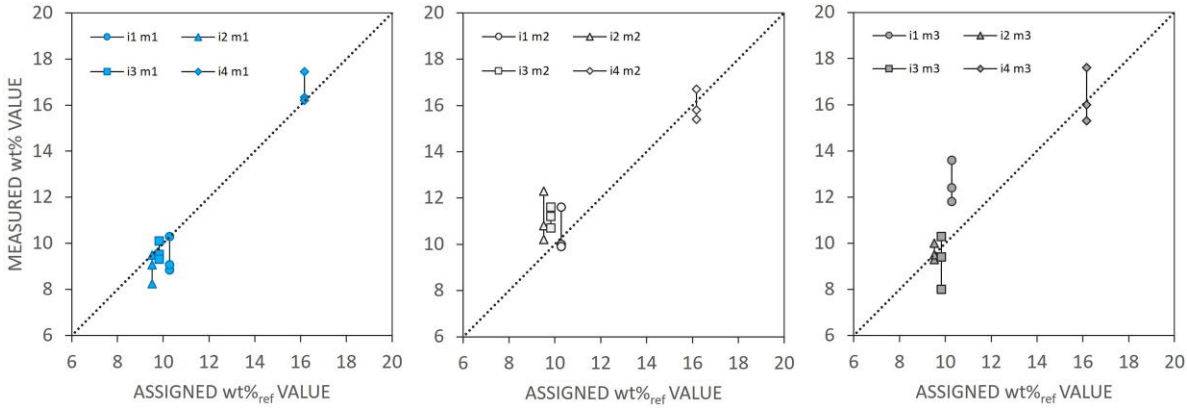

Fig. 1. Results from laboratory no. 1 for measurements under repeatability conditions, compared with assigned values ($m = 1$ method for specimen on filter; $m = 2$ internal standard method; $m = 3$ spiking method).

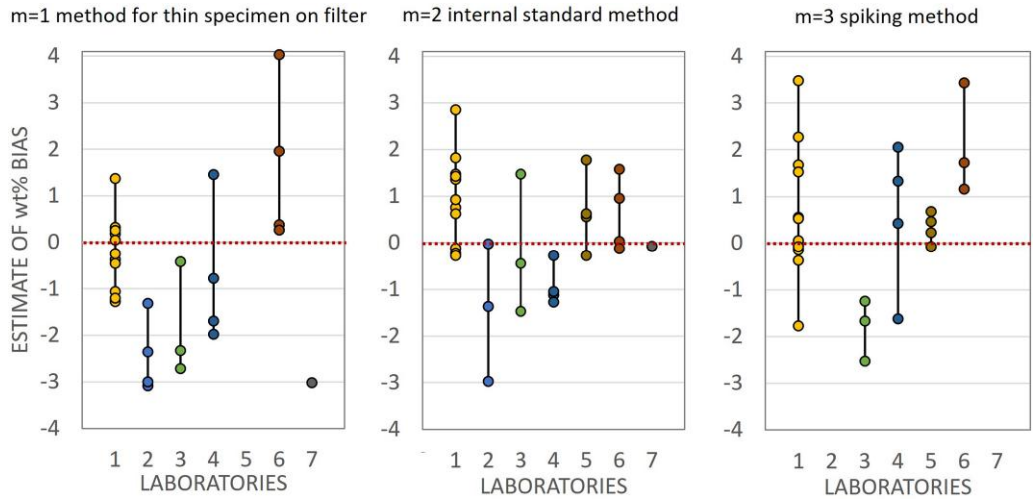

Fig. 2. Estimate of bias from all the laboratories for the 3 methods at both levels.

analyses by the 3 methods, so some test results are missing. Application of Grubbs' test to the test results found one outlier in both the internal standard method and the spiking method data sets. These 2 test results were rejected.

Table 3 shows the outcomes of the experiment, ie the estimate of repeatability and reproducibility SDs and bias of the measurement methods.

The accepted reference values are $wt\%_{\mathrm{ref},i1} = 10.1$ (quartz-baryte mixture), $wt\%_{\mathrm{ref},i2} = 9.4$ (quartz-calcite mixture), and $wt\%_{\mathrm{ref},i3} = 9.8$ (quartz-talc mixture), so that an average value of 9.8 quartz percent weight represents level $y1$. Sample 4 (quartz-anorthite mixture) accepted reference value is $wt\%_{\mathrm{ref},i4} = 16.1$, which also represents level $y2$.

Measurements under repeatability conditions (3 independent analyses on each sample by all the 3 methods) were carried out only in laboratory no. 1, and the results are shown in Fig. 1.

Figure 2 shows the bias values for each laboratory with each method, while the estimates of bias at levels 1 and 2 are plotted in Fig. S2 in the Supplementary materials.

The measurement results for quartz percent weight wt% of each sample and each method are given in the box-plots of Fig. 3.

Table 4 shows the results of the F-tests conducted to test if there is evidence that the methods have different within-laboratory precision and overall precision, and the results of the comparisons between the grand means of the methods, to verify if the differences are statistically significant.

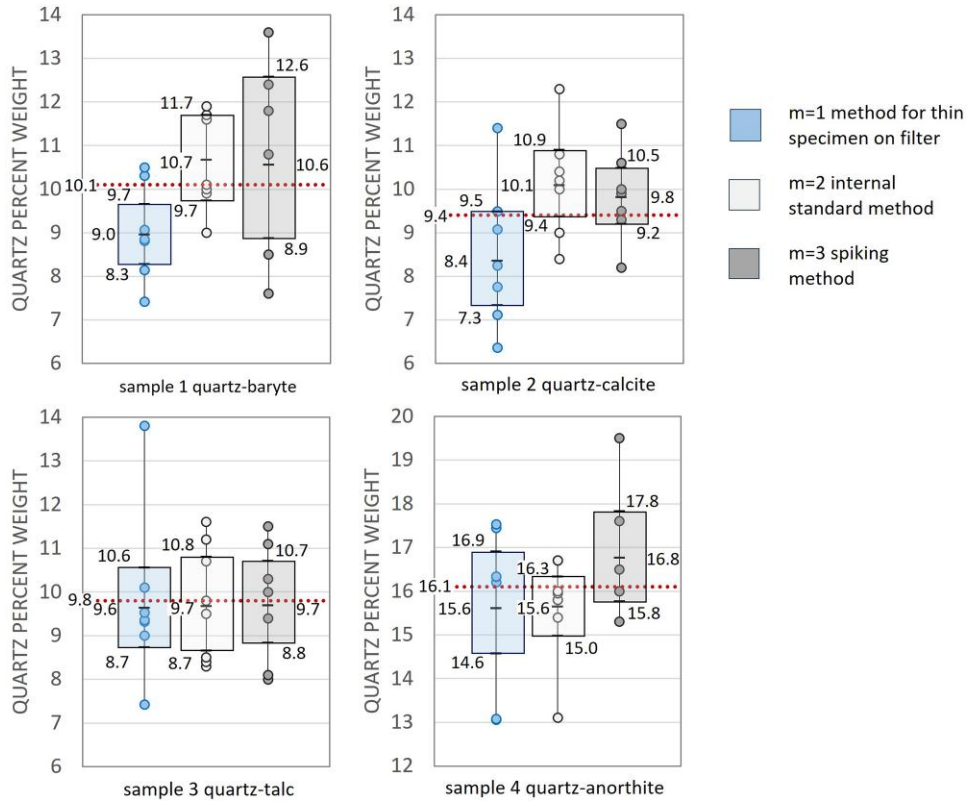

Fig. 3. Box-plots for the distribution of sets of data of the 4 samples analysed by the 3 methods. The dotted line shows the accepted reference value. The box plot is divided into quartiles and a short line marks the median (their wt% values are shown).

Table 4. Comparisons of precision and between the means of measurement methods (A and B represent each pair of methods under comparison).

Compared methods	Method for thin specimen on filter and internal standard method	Method for thin specimen on filter and spiking method	Internal standard method and spiking method
	Comparison of precision		
	Within-laboratory precision		
F_r	1.86	1.78	1.04
$F_{\alpha/2(\nu_{r,mA},\nu_{r,mB})}$	3.37	3.72	3.37
$F_{(1-\alpha/2)(\nu_{r,mA},\nu_{r,mB})}$	0.30	0.27	0.30
	Overall precision		
F_R	2.29	1.91	2.13
$F_{\alpha/2(\nu_{R,mA},\nu_{R,mB})}$	3.62	3.72	3.62
$F_{(1-\alpha/2)(\nu_{R,mA},\nu_{R,mB})}$	0.28	0.27	0.28
	Comparison between the means		
$\left\lvert\frac{\overline{\overline{wt\%}}_{mA,y}-\overline{\overline{wt\%}}_{mB,y}}{\sqrt{s^2_{mA}+s^2_{mB}}}\right\rvert$	1.33	1.04	0.09

Discussion and conclusion

General considerations

X-ray powder diffraction allows mineral phases to be identified and quantified based on their unique crystal structures, enabling individual crystalline phases to be distinguished from amorphous materials. It is therefore the preferred technique when it is necessary to distinguish quartz from other crystalline silica phases and amorphous forms. The XRD technique is known to

be affected by many factors that decrease its accuracy, and the variance of results is generally larger than that of other analytical techniques used to determine the chemical composition of materials (Madsen et al. 2019). However, these other chemical methods are not sufficiently specific for the quantification of the crystalline form of silica.

The 3 traditional XRD methods included in the inter-laboratory experiments described in this paper were used to determine the abundance of a single mineral phase, quartz, by measuring its 3 most intense peaks in 4 binary mixtures. These methods are potentially more difficult to use when all the measured intensities have interference compared with full pattern methods like Rietveld that are potentially able to adjust for coincident intensities. On the other hand, they do not require the identification of matrix composition and the determination of phase crystal structures and are generally less demanding in terms of working time and the analyst's skills with respect to whole-pattern methods.

There are several factors that can cause larger or smaller deviations in the quantification of quartz when determined by the methods described in this paper. Some of these parameters are fundamentally theoretical; others are more uncertain but can be conjectured. Among these parameters, we mainly consider:

(i) Errors related to the absorption effect, which may be applied or not when using the spiking method.
(ii) Errors related to the sample preparation including: (i) weighing errors due to mixing small amounts of internal standard (RIR method) or quartz reference material (spiking method); (ii) proper mixing of sample with the internal standard material; (iii) contamination during sample preparation: quartz is an omnipresent mineral and a main component of many natural/artificial materials; (iv) the sample grinding procedure, with decrease in quartz crystallinity, and thus XRD intensity, and other effects; (v) the mounting of powder sample in the sample holder, and the preferential orientation (internal standard method, spiking method); (vi) sample treatment for removal of interfering phases; and (viii) for the filter method: the loss of powder from the filter before analysis; the uneven distribution of powder deposited on the filter and the differences in powder distribution between the calibration filters and the sample filters; preferential orientation.
(iii) Errors related to the determination of the corrected or uncorrected intensity of a quartz peak: (i) Is the area determined by the sum of the absolute intensities between the measured peak and the background? Or is the peak modelled and the area of the modelled peak used to determine the intensity?; (ii) background modelling: is a straight line used or a polynomial and if so, which degree of polynomial is being used?; (iii) different crystallite sizes between quartz in sample and the spiked quartz reference material (in case a modelled peak area is used); (iv) long-term intensity drift due to the decrease in emitted X-rays over time (internal standard method, filter method); (v) choice of the right peak—free of interferences: if the largest quartz peak shows peak overlap, another quartz peak has to be chosen. Nonetheless, smaller quartz peaks may be influenced even more by small overlapping reflections; (vi) the procedure for intensity correction in the presence of small interferences (all the methods); (vii) the different 2Theta interval used in different samples for measuring the intensity of a peak (all the methods).
(iv) Finally, operator errors in some steps of the analysis could be an important source of error, as it was found in other round-robins (Madsen et al. 2019). It should be noted that while all the laboratories participating in the round-robin had considerable experience with XRD analysis of respirable dust deposited on filters, some of the laboratories had very limited experience with XRD analysis of bulk samples, and the round-robin was a learning experience.

Some of these parameters may be quantified (eg weighing errors), but the influence of the individual contributions is difficult to assess, as the described effects may also vary quantitatively (eg with preferred orientation).

The boxplot of Fig. 3 shows the results for quartz percent weight wt% of each sample and each method. The analyses carried out on filters indicate a general underestimation of quartz when in a mixture with baryte or calcite. Calcite and especially baryte show the greatest absorption coefficient difference with respect to quartz, so the slight underestimation when the method for the deposition on a filter is applied to mixtures of quartz with highly absorbing phases could be due to an insufficient correction of absorption (by the transmission method for correction). Conversely, quartz content results for the same quartz-baryte and quartz-calcite mixtures generally show an overestimation when the internal standard method is used. This slight but systematic overestimation in the content of low-absorbing quartz might possibly be due to micro-absorption effects due to the presence of relatively larger particle sizes in the mixture of quartz with baryte or calcite, or could be related to some effect due to the difference in grain size between quartz and the other mineral in the binary mixture. Analyses performed with the spiking method on samples of quartz mixed with a high-absorbing phase, such as baryte, should give percent contents of quartz lower

than the true values when the additions of quartz dopant to the specimens are large enough to cause important changes in their mass absorption coefficients. However, this effect was not observed in the results of the interlaboratory comparison.

The issue of crystallinity value assigned to a quartz reference material has been outlined in the methods section. In fact, different quartz reference materials produce different diffraction intensities. Therefore, mistaken evaluations of quartz crystallinities will produce calibration lines with different slopes and the same sample analysed in different laboratories will yield different quartz contents. Different effects are produced with the 3 methods if the crystallinity of the quartz reference material used for calibration (or added to a specimen) is not considered or incorrectly estimated.

When using the external standard method for samples of powder deposited on filters, a crystallinity overestimation produces quartz measurements that are proportionally higher than the true value. A similar effect also occurs when using the spiking method. However, in this case, the effect only affects the specimens doped with quartz additions and not the specimens without quartz addition, which is also part of the set of specimens (usually 3) analysed by this method. The result of the quartz determination will therefore be higher than the true value, but less than that with the method for samples on filters. In the internal standard method, a quartz reference material is used by a laboratory in the preparation of a 50%:50% mixture with an internal standard, to be used for the determination of the RIR value. Clearly, an overestimation of crystallinity of that quartz RM implies that the weight fraction of quartz, w% in Eq. 5, actually present in the mixture with the internal standard will be less than 50%, affecting the value of the calculated RIR. Therefore, an overestimation of the crystallinity of the quartz reference material will produce a proportional underestimation of the results obtained for quartz in all the samples analysed by the laboratory.

Comparison with round robin data

In the last 25 yr, a number of round-robins have been conducted on the determination of quantitative phase abundance from diffraction data, on bulk samples made of multi-phase mixtures in known proportions, with most of them analysed by a Rietveld method. The papers published by Madsen et al. (2001), Scarlett et al. (2002), León-Reina et al. (2009), and Fawcett et al. (2010) report the results obtained by each laboratory for the percentage weight content of all the phases present in each sample. These data were used to calculate the SDs of the mean at different concentration levels. The characteristics of round-robins, the number of participating laboratories, the test samples number and phase compositions are described in the supplementary material (Table S1). Even though they were designed with different objectives, comparing the SDs of their results with those from the interlaboratory experiment in this work provides important context.

The average SDs at the 10% wt concentration level of a phase were found to be approximately 1.5% in the analyses of both Portland cements (León-Reina et al. 2009) and samples prepared from artificial mixtures of corundum, fluorite, and zincite (Madsen et al. 2001). At the wt%≈16 level, the SDs from the same round-robins were 1.8 to 2.0 and 2.0, respectively. In the round-robin study published by Scarlett et al. (2002), samples of synthetic bauxite and natural granodiorite included quartz in concentrations of approximately 5% and 30%, respectively. At these concentration levels, the SDs were 1.3% and 7.4%, essentially the same as those obtained in the round-robin study by Madsen et al. (2001) (see Table S1 in the supplementary material). The values of the SD of the mean reported above are in the same range as the reproducibility SDs obtained in this study, using all 3 proposed methods for quartz at the same wt% concentration levels (Table 3). Much higher SD values, in the range 14% to 18% at the 16% wt concentration level, have been calculated from the results published by Fawcett et al. (2010) for a round-robin on challenging mixtures of pharmaceuticals and a silicon reference material.

Performance and comparability of the 3 analytical methods

Standardization of methods can lead to better agreement between results from different laboratories, especially when the experience of some laboratories is limited. The publication of this round-robin and of the ISO standard is a first step towards achieving this.

The accepted reference values of quartz percent content in the 4 samples (Table 3), calculated as the mean values from all the valid measurements, as described in the statistical method section, were close to the expected values based on the amounts of quartz reference material included in the mixtures.

The precision of each measurement method, as a percentage of quartz weight in a sample, is expressed in terms of repeatability SD, s_r (or relative SD, RSD_r), and reproducibility SD, s_R (or relative SD, RSD_R).

The repeatability SDs calculated for the 10 to 16 wt % quartz range were found similar for the 3 XRD methods: between 0.4 and 0.8 (RSD_r between 4.3% and 8.7%) for thin specimens on filters, 0.4 to 1.1 (RSD_r between 4.2% and 10.6%) for the internal standard method, and 0.3 to 1.2 (RSD_r between 3.7% and 11.9%) for the spiking method (Table 3). Figure 1 shows the repeatability results in Lab. 1

compared with the values assigned to the 4 samples. An average 5% underestimation of wt% was found when using the method for thin specimens, $m = 1$, on filters at the level of wt% $\approx$ 10, while an average 11% overestimation of wt% was found for the internal standard method, $m = 2$, at the same level. Results for analyses with the spiking method, $m = 3$, fluctuated around the assigned value except for the quartz-baryte sample where a consistent overestimation (23% on average) was observed.

The reproducibility SD of the results of measurements in the studied wt% range, from all the laboratories, were between 1.1 and 2.1 (RSD_R between 12.7% and 21.5%) for the method of thin specimen on filter, 1.1 to 1.4 (RSD_R between 7.5% and 14.1%) for the internal standard method and 1.1 to 2.6 (RSD_R between 9.5% and 23.7%) for the spiking method (Table 3). These SDs are in the same range as those calculated at the same concentration levels of different phases analysed in other round-robins for quantitative XRD phase analysis.

The estimates of weight percent bias shown in Fig. 2 allow for an evaluation of the performance of each laboratory with the 3 methods. A consistent overestimation or underestimation of the target value was found for most of the laboratories with at least one of the methods.

The aim of this study was also to demonstrate the statistical equivalence of the 3 analytical methods for the determination of quartz percent content in bulk samples.

The outcomes of the F tests shown in Table 4 show that the variances of the 3 methods are equal at the $\alpha = 5\%$ significance level, and the differences between the grand means of the test results of the methods tested in all the laboratories are statistically insignificant. This comparability study was conducted only at the concentration levels wt% $\approx$ 10 and wt% $\approx$ 16. Therefore, it would be important to test the 3 methods using real samples over a wider quartz concentration range.

The estimates of the bias of the measurement methods obtained from laboratories' results are given in Table 3 and Fig. 3. An approximate 95% confidence interval for the bias of each measurement method is also shown in Table 3. Since at concentration levels wt% = 10 and wt% = 16 the confidence intervals of all the 3 methods cover the value zero, the biases of the 3 methods of measurements are insignificant at the significance level $\alpha = 5\%$ in the studied concentration range, also supporting the finding that these 3 methods produce statistically equivalent results at the 2 concentration levels studied.

It is clear that if these methods of analysis were to be used to ascertain compliance with the requirements of the regulations for the classification and labelling of chemicals, they would also have to be tested at the low concentration levels indicated in the introduction. Further investigations into the capability of these methods to quantify crystalline silica in bulk samples at low levels are needed before these methods can be used to quantify crystalline silica at the threshold values applied for regulatory purposes in some countries, eg 1% and 0.1%.

Acknowledgments

We would like to acknowledge Matthew Jackson and James Staff who conducted the quality control tests for sample 4 and Margaret Wade and Susan Hambling for their reviews at the Health and Safety Executive.

Supplementary material

Supplementary material is available at *Annals of Work Exposures and Health* online.

Funding

The contribution of each author was funded by their respective institution. No additional source of funding was used for this work.

Conflict of interest

The authors declare no conflict of interest relating to the material presented in this Article. Its contents, including any opinions and/or conclusions expressed, are solely those of the authors and do not necessarily reflect policy of any national regulatory authority.

Data availability

All the data underlying this article are available in the article.

References

Altree-Williams S. 1977. Quantitative X-ray diffractometry on milligram samples prepared on silver filters. Anal Chem. 49:429–432. https://doi.org/10.1021/ac50011a025.

Blount AM, Carr FP. 1994. Determining a viable X-ray diffraction technique for routine quantification of the quartz content of powdered carbonates. Anal Chim Acta. 286: 117–123. https://doi.org/10.1016/0003-2670(94)80183-5.

Carter JR, Hatcher MT, Di Carlo L. 1987. Quantitative analysis of quartz and cristobalite in bentonite clay based products by X-ray diffraction. Anal Chem. 59:513–519. https://doi.org/10.1021/ac00130a030.

Clarke FW. 1924. The data of geochemistry. 5th ed. U.S. Geol. Surv. Bull. 770: page 33.

Elton NJ, Smith DK. 1999. Silica. In: Chung FH, Smith DK, editors. Industrial applications of X-ray diffraction. 1st ed. Taylor & Francis. p. 441–470.

Emig JA, Smith DK. 1989. The detection and quantification of low concentrations of quartz in dolostone by X-ray powder diffraction. Powder Diffr. 4:209–213. https://doi.org/10.1017/S0885715600013749.

Fawcett TG, Needham F, Faber J, Crowder CE. 2010. International centre for diffraction data round robin on quantitative Rietveld phase analysis of pharmaceuticals. Powder Diffr. 25:60–67. https://doi.org/10.1154/1.3312754.

Gordon RL, Harris GW. 1955. Effect of particle-size on the quantitative determination of quartz by X-ray diffraction. Nature. 175:1135. https://doi.org/10.1038/1751135a0.

Hardy M. 1992. X-ray diffraction measurement of the quartz content of clay and silt fractions in soil. Clay Miner. 27: 47–55. https://doi.org/10.1180/claymin.1992.027.1.05.

Horwitz W. 1995. Protocol for the design, conduct and interpretation of method-performance studies. Pure Appl Chem. 67: 331–343. https://doi.org/10.1351/pac199567020331.

HSE. 2022. A9950 respirable α-quartz powder reference material —certificate of analysis. Health and Safety Executive.

Hurst JA. 2012. Determination of quartz in bulk materials from workplace environments using X-ray diffractometry and the absorption diffraction method. Talanta. 93:392–397. https://doi.org/10.1016/j.talanta.2012.02.060.

ISO 16258-2:2015. Workplace air—Analysis of respirable crystalline silica by X-ray diffraction—Part 2: Method by indirect analysis.

ISO 5725-1:2023. Accuracy (trueness and precision) of measurement methods and results—Part 1: General principles and definitions.

ISO 5725-2:2019. Accuracy (trueness and precision) of measurement methods and results—Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method.

ISO 5725-4:2020. Accuracy (trueness and precision) of measurement methods and results—Part 4: Basic methods for the determination of the trueness of a standard measurement method.

ISO 5725-6:1994. Accuracy (trueness and precision) of measurement methods and results—Part 6: Use in practice of accuracy values.

Jordan B, O'Connor BH, Deyu L. 1990. Use of Rietveld pattern fitting to determine the weight fraction of crystalline material in natural low quartz specimens. Powder Diffr. 3:64–69. https://doi.org/10.1017/S0885715600015359.

Kauffer E et al. 2002. Comparison by X-ray diffraction and infrared spectroscopy of two samples of α quartz with the NIST 1878a α quartz. Ann Occup Hyg. 46:409–421. https://doi.org/10.1093/annhyg/mef050.

Klug HP, Alexander LE. 1974. X-Ray diffraction procedures for polycrystalline and amorphous materials. 2nd ed. Wiley.

León-Reina L et al. 2009. Round robin on Rietveld quantitative phase analysis of Portland cements. J Appl Cryst. 42: 906–916. https://doi.org/10.1107/S0021889809028374.

Liu B, Pui D, Rubow K. 1983. Characteristics of air sampling filter media. In: Marple VA, Liu B, editors. Aerosols in the mining and industrial work environments. Ann Arbor Science. p. 989–1002

Madsen IC, Scarlett NVY, Cranswick LMD, Lwin T. 2001. Outcomes of the international union of crystallography commission on powder diffraction round robin on quantitative phase analysis: samples 1a to 1h. J Appl Cryst. 34: 409–426. https://doi.org/10.1107/S0021889801007476.

Madsen IC, Scarlett NVY, Kleeberg R, Knorr K. 2019. Quantitative phase analysis. In: Gilmore CJ, Kaduk JA, Schenk H, editors. International tables for crystallography, Vol. H, powder diffraction. 1st ed. Chester. p. 344–373

Mandel J. 1964. The statistical analysis of experimental data. Interscience Publishers—J. Wiley & Sons.

Martin J, Beauparlant M, Lesage J, Van Tra H. 2012. Development of a quantification method for quartz in various bulk materials by X-ray diffraction and the Rietveld method. Powder Diffr. 27:12–19. https://doi.org/10.1017/S0885715612000036.

NIOSH. 1994. Silica, crystalline, by XRD (filter redeposition): method 7500. In: Eller PM, editor. NIOSH Manual of analytical methods. 4th ed. NIOSH—National Institute for Occupational Safety and Health. p. 9.

NIST. 2005. Standard reference material 1878a—respirable alpha quartz for quantitative X-ray powder diffraction—certificate of analysis. NIST, U.S. Department of Commerce.

NIST. 2017. Standard reference material 1878b—respirable alpha quartz for quantitative X-ray powder diffraction—certificate of analysis. NIST, U.S. Department of Commerce.

Radnoff DL, Kutz MK. 2014. Exposure to crystalline silica in abrasive blasting operations where silica and non-silica abrasives are used. Ann Occup Hyg. 58:19–27. https://doi.org/10.1093/annhyg/met065.

Renault J, McKee C, Barker J. 1994. New X-ray diffraction method of additions for crystalline silica. Anal Chim Acta. 286: 129–133. https://doi.org/10.1016/0003-2670(94)80185-1.

Salt PD. 1985. Quantitative mineralogical analysis of small samples of China clay using X-ray diffractometry. Br J Ind Med. 42:635–641. https://doi.org/10.1136/oem.42.9.635.

Salter TL, Riley W. 1994. Quartz determination in kaolin at the 0.1% level. Anal Chim Acta. 286:49–55. https://doi.org/10.1016/0003-2670(94)80175-4.

Scarlett NVY et al. 2002. Outcomes of the international union of crystallography commission on powder diffraction round robin on quantitative phase analysis: samples 2, 3, 4, synthetic bauxite, natural granodiorite and pharmaceuticals. J Appl Cryst. 35:383–400. https://doi.org/10.1107/S0021889802008798.

Smith DK. 1997. Evaluation of the detectability and quantification of respirable crystalline silica by X-ray powder diffraction methods. Powder Diffr. 12:200–227. https://doi.org/10.1017/S0885715600009775.

Stacey P et al. 2009. An international comparison of the crystallinity of calibration materials for the analysis of respirable α-quartz using X-ray diffraction and a comparison

with results from the infrared KBr disc method. Ann Occup Hyg. 53:639–649. https://doi.org/10.1093/annhyg/mep038.

Stacey P. 2019. A study to assess the performance of an "X-ray powder diffraction with Rietveld" approach for measuring the crystalline and amorphous components of inhalable dust collected on aerosol sampling filters. Powder Diffr. 34: 251–259. https://doi.org/10.1017/S0885715619000423.

Taylor M. 1978. Methods for the quantitative determination of asbestos and quartz in bulk samples using X-ray diffraction. Analyst. 103:1009–1020. https://doi.org/10.1039/an9780301009.

Tomaino GP. 1994. Quantitative determination of quartz in calcite, dolomite, and talc by powder X-ray diffraction analysis. Anal Chim Acta. 286:75–80. https://doi.org/10.1016/0003-2670(94)80178-9.