

R. DETERMINATION OF AIRBORNE CRYSTALLINE SILICA

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1. INTRODUCTION

A variety of air sampling and analysis methods for determining workers' exposures to crystalline silica have been published by the National Institute for Occupational Safety and Health (NIOSH), the Occupational Safety and Health Administration (OSHA), the Mine Safety and Health Administration (MSHA), the United Kingdom Health and Safety Executive (UK-HSE) and others. The following chapter provides information on the structure of silica, health effects, airborne exposure standards, sampling considerations and analytical considerations. The purpose is to provide information to the industrial hygienist, chemist, laboratory manager and the client of laboratory services to make an informed decision on which crystalline silica method should be used, and the quality assurance procedures that should be employed to obtain accurate results.

2. STRUCTURE, PROPERTIES AND OCCURRENCE OF SILICA

Silica is commonly found in the earth's crust and refers to the chemical compound silicon dioxide (SiO<sub>2</sub>). Physical properties (such as specific gravity, refractive index and X-ray diffraction pattern) and toxicological properties depend on the chemical composition and the molecular structure. Silica occurs in both crystalline and non-crystalline forms. Crystalline forms are physical states in which the silicon dioxide molecules are arranged in a repetitive pattern that has unique spacing, lattice structure and angular relationship of the atoms. Crystalline silica forms (often referred to as polymorphs) include quartz, cristobalite, tridymite, keatite, coesite, stishovite and moganite [2,3,4]. Figure 1 shows the lattice arrangements of quartz, cristobalite and tridymite. Table 1 lists some physical properties of these polymorphs.

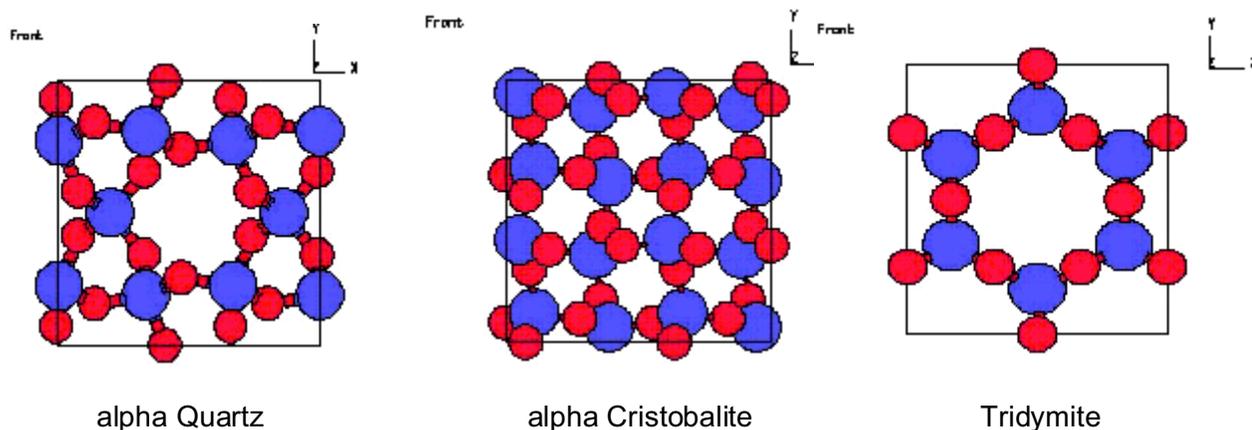


Figure 1. Polymorphs of crystalline silica [5].

**TABLE 1. PHYSICAL PROPERTIES OF QUARTZ, CRISTOBALITE AND TRIDYMITE.**

Silica Polymorph	Crystal Structure	Index of Refraction	Specific Gravity	Other Properties
Quartz	hexagonal	1.544	2.645 - 2.660	Mol.Wt. 60.08 m.p. °C 1610
Cristobalite	cubic or tetragonal	1.487	2.32	Mol.Wt. 60.08 m.p. °C 1723
Tridymite	rhombohedral	1.469	2.26	Mol.Wt. 60.08 m.p. °C 1703

In nature, quartz is the crystalline form most commonly encountered and is so abundant that the term quartz is often used in place of the general term crystalline silica [6, 7]. Quartz is abundant in most rocks and soils and is also present in sand, mortar, concrete, fluxes, abrasives, construction aggregate, porcelain, paints and brick [8]. In addition, quartz-containing dust may be generated in any process which involves movement of earth (e.g., mining, farming, construction), disturbance of silica-containing products such as masonry and concrete, or use of sand and other silica containing products (e.g., foundry processes). Consequently, workers are potentially exposed to quartz dust in many occupations and industries.

Cristobalite and tridymite can be found in volcanic rocks and soils. These polymorphs can also be produced in some industrial operations. For example, cristobalite transformations occur in foundry processes, calcining of diatomaceous earth, brick and ceramics manufacturing, and silicon carbide production [9-11]. Burning of agricultural waste or products such as rice hulls may also cause amorphous silica to become cristobalite [8,12].

The other crystalline polymorphs (i.e., keatite, coesite, stishovite, and moganite) are very rarely or never observed in nature and are formed only under very high pressures [2]. Since these polymorphs are generally formed in small quantities, they are therefore of limited industrial hygiene interest.

Non-crystalline, or amorphous, forms of silica exist when the silicon dioxide molecules are randomly arranged. Fly ash, silica fume and silica gel contain amorphous silica. Diatomaceous earth is 88% amorphous silica and is composed of the skeletons of small prehistoric aquatic plants related to algae [13]. Sometimes the compound may be hydrated, such as in opal.

Silica (both amorphous and crystalline) can transform. In unusual instances of extreme heat and very slow cooling conditions, amorphous silica can be transformed into crystalline silica as mentioned above. Similarly, various crystalline silica forms can transform into different crystalline forms when subjected to high heat or high heat and pressure. The presence of trace elements in the silica affects transformation rates. Heating rate is also important; on heating, cristobalite may form without first forming tridymite. Figure 2 illustrates some transitions between forms of silica upon heating and cooling.

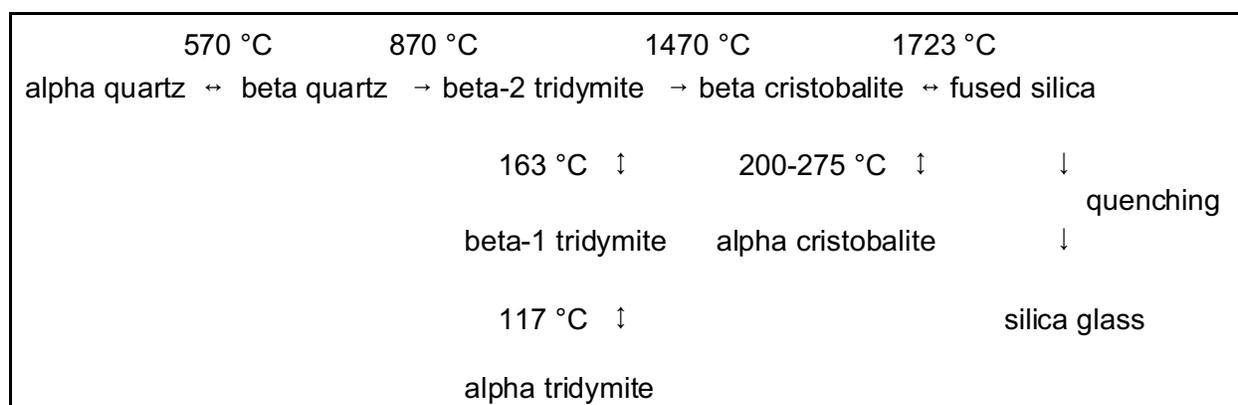


Figure 2. Silica transitions with temperature [8].

### 3. HEALTH EFFECTS AND EXPOSURE STANDARDS

At least 1.7 million U.S. workers are potentially exposed to crystalline silica, which can cause the debilitating and incurable, but entirely preventable, lung disease called silicosis. Reported mortality associated with silicosis has declined to 200 to 300 reported deaths each year during the period 1992-1995. However, silicosis remains under-reported, perhaps because of a long latency between exposure and disease. In addition, an unknown number of unreported or undiagnosed worker deaths occur each year from silicosis and other silica-related diseases such as pulmonary tuberculosis (TB), lung cancer, and scleroderma. Occupational exposure to respirable crystalline silica is associated with the development of silicosis, lung cancer, pulmonary tuberculosis and airways diseases. These exposures may also be related to the development of autoimmune disorders, chronic renal disease and other adverse health effects [14].

In 1974, NIOSH reviewed the available health effects data on occupational exposure to respirable crystalline silica and determined that the principal adverse health effect was silicosis [9]. On the basis of the evidence from the animal studies published by 1986, the International Agency for Research on Cancer (IARC) concluded that “sufficient evidence” existed for the carcinogenicity of respirable crystalline silica in experimental animals but only “limited evidence” existed for carcinogenicity in humans [15]. During the 1988 OSHA rule-making activity on air contaminants, NIOSH recommended an exposure limit of 0.05 mg/m<sup>3</sup> “as respirable free silica for all crystalline forms of silica” to protect workers from silicosis and cancer [16]. In addition, NIOSH testimony referred to the IARC [1987] review and recommended that OSHA label crystalline silica a potential occupational carcinogen [16]. IARC recently concluded that there is “sufficient evidence in humans for the carcinogenicity of inhaled crystalline silica in the form of quartz or cristobalite from occupational sources” (i.e., IARC category Group 1 carcinogen) [8]. The American Conference of Governmental Industrial Hygienists (ACGIH) has classified crystalline silica as a “suspected human carcinogen” (i.e., category A2 carcinogen) [17]. The National Toxicology Program reclassified respirable crystalline silica from “reasonably anticipated to be a carcinogen” to “known carcinogen” in the 9<sup>th</sup> Report on Carcinogens [18]. Furthermore, experimental research has shown that crystalline silica is not an inert dust. The toxicity of crystalline silica particles may be related to reactive sites on the surfaces of silica particles and the crystallinity index [19]. Table 2 lists the current U.S. and U.K. guidelines and limits for occupational exposure to crystalline silica.

**TABLE 2. U.S. AND U.K. GUIDELINES AND LIMITS FOR OCCUPATIONAL EXPOSURE TO CRYSTALLINE SILICA.**

Reference	Substance	Guideline or limit (mg/m <sup>3</sup> )
NIOSH [ 9]	Crystalline silica: quartz, cristobalite and tridymite as respirable dust	REL = 0.05 (for up to a 10-h workday during a 40-h workweek)
OSHA [29 CFR 1910.1000-Table Z-3] <sup>†</sup> CFR [20]	dust (respirable) containing quartz dust (respirable) containing cristobalite  dust (respirable) containing tridymite	8-h TWA PEL = 10 ÷ (% quartz + 2) PEL = half of the value calculated from the formula for dust-containing quartz PEL = half of the value calculated from the formula for dust-containing quartz
MSHA [30 CFR 56, 57, 70, 71] CFR [20]	dust (respirable) containing > 1% quartz in surface and underground metal and nonmetal mines dust (respirable) containing > 1% cristobalite or tridymite in surface and underground metal and nonmetal mines dust (total) containing < 1% crystalline silica in surface and underground metal and nonmetal mines dust (respirable) containing >5% crystalline silica in surface and underground coal mines dust (respirable) containing ≤ 5% crystalline silica in surface and underground coal mines	8-h TWA TLV = 10 ÷ (% quartz + 2)  8-h TWA TLV = 5 ÷ (% SiO <sub>2</sub> + 2)  8-h TWA TLV = 10 (for particulates listed in Appendix E, 1973 ACGIH TLVs only) TWA RDS = 10 ÷ % SiO <sub>2</sub> (MRE equivalent)  TWA RDS = 2 (MRE equivalent)
ACGIH [17]	Respirable crystalline silica, quartz Respirable crystalline silica, cristobalite Respirable crystalline silica, tridymite	8-h TWA TLV = 0.05 8-h TWA TLV = 0.05 8-h TWA TLV = 0.05
UK-HSE [21, 22, 23]	Respirable crystalline silica, total (quartz + cristobalite)	8-h TWA MEL = 0.300

Adapted from Hehl [24].

\*Identified by NIOSH as a potential occupational carcinogen [16].

<sup>†</sup>See this website for sample calculations of the OSHA PEL: [http://www.osha-slc.gov/SLTC/silica\\_advisor/mainpage.html](http://www.osha-slc.gov/SLTC/silica_advisor/mainpage.html). Other useful information is available on this website: <http://www.osha-slc.gov/SLTC/silicacrystalline/rosem/index.html>. On this web page, click on "Frequently Asked Questions."

CFR = Code of Federal Regulations; REL = recommended exposure limit; PEL = permissible exposure limit; TWA = time-weighted average; RDS = respirable dust standard; MRE = Mining Research Establishment (United Kingdom); TLV = threshold limit value; MEL = maximum exposure limit.

Under the OSHA Hazard Communication Standard (HCS) materials containing 0.1% or more crystalline silica by weight must follow federal guidelines concerning hazard communication and worker training [6, 8, 16]. Although HCS does not require the analysis of materials for crystalline silica content, material suppliers or employers may want to have materials analyzed for crystalline silica to be exempt from HCS requirements. Unfortunately, laboratories may need to deal with clients that assume a low concentration of a commonly occurring mineral like crystalline silica can be measured reliably and accurately. Sample inhomogeneity, measurement sensitivity and specificity limitations when other minerals are present make it difficult if not impossible for a laboratory to provide the conclusive evidence that laboratory clients seek to avoid HCS requirements.

#### 4. SAMPLING CONSIDERATIONS

Current methods for sampling airborne silica use a cyclone with a cassette to collect the respirable fraction of the aerosol. To minimize measurement bias and variability, these samplers should conform to the criteria of the International Organization for Standardization (ISO), the European Standardization Committee (CEN), and the American Conference of Governmental Industrial Hygienists (ACGIH) for collecting particles of the appropriate size [25, 26, 27]. Also, the cyclone should exhibit sufficient electrical conductivity to minimize the electrostatic effects on particle collection.

Cyclones typically used for crystalline silica measurements include the non-conductive Dorr-Oliver 10-mm nylon cyclone and the conductive Higgins-Dewell cyclone. These cyclones have been evaluated for their compliance with the ISO/CEN/ACGIH respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver cyclone and 2.2 L/min for the Higgins-Dewell cyclone provide minimum bias for a wide range of particle size distributions that is likely to occur in the workplace [28]. The Dorr-Oliver 10-mm cyclone is the approved sampler for MSHA (CFR 30 Parts 70.100-10.206 and 71.100-71.206) and is commonly used in the United States, while the Higgins-Dewell cyclone is used in the United Kingdom and is sold in the United States and Canada. (Though the sampling recommendations to adopt the ISO/CEN/ACGIH respirable sampling convention have been formally accepted by MSHA for coal mine dust sampling, MSHA currently requires the use of the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor to match an earlier sampling convention (British Medical Research Council [BMRC], 1961) [29].

Recently, the BGI GK2.69 cyclone [30] has become commercially available with a sampling rate equal to 4.2 L/min. The GK2.69 cyclone is expected to be at least as adequate as the nylon cyclone for conforming to the ISO/CEN/ACGIH respirable aerosol sampling convention; and it may be preferable for silica sampling since it is conductive, has well-defined dimensional characteristics and can be used at higher flow rates to achieve a lower detection limit. Given that current analysis methods do not have sufficient accuracy to monitor below current exposure standards, this sampler has promise for potentially lowering the levels of silica that can be measured and still meet the required measurement accuracy. The availability of a pre-selector such as the GK2.69 cyclone sampler, which is designed to conform to the respirable dust sampling criteria at a flow rate nearly two and a half times that of the nylon cyclone, offers the field industrial hygienist the ability to collect a quantifiable sample mass during tasks of short duration or of low dustiness, conditions which may not have yielded a quantifiable mass using the nylon cyclone. The hygienist must be mindful of such things as ambient conditions, analytical detection limit, working analytical range and required air volume when selecting the appropriate sampler.

Each type of cyclone exhibits its own unique particle collection characteristics and the three major methods of analysis (XRD, IR, and colorimetric) are subject to different particle size effects. Therefore, the use of a single cyclone type for each application is advised until evidence becomes available indicating that bias among cyclone types will not increase inter-laboratory variability. In practice, the Dorr-Oliver 10-mm nylon cyclone has been used since the 1960's and has been a basis for some epidemiological studies. While augmenting the list of recommended samplers with the Higgins-Dewell and the BGI GK2.69 cyclones would

allow better sensitivity in samples taken with them, interlaboratory precision would suffer due to the use of multiple sampling devices. At this time, silica sampling should be done with a 1.7 L/min Dorr-Oliver nylon cyclone to meet the ISO/CEN/ACGIH respirable sampling convention within the United States. A future change to the GK2.69 sampler is a possibility.

Both cyclones and filter cassettes should be leak-tested prior to sampling to avoid gross failure in the field [31,32]. The cyclones may be tested using a simple pressure- (or vacuum-) holding test. The filter cassette should also be checked for leakage while attached to the cyclone. Two approaches to testing the cassettes have been used. One approach used a micromanometer to measure pressure drop across a given cassette and compared it to the average pressure drop across well-sealed cassettes [33]. An alternative approach used a particle counter to measure the penetration of submicrometer ambient aerosol through the cassette, with the percentage of penetration serving as an indicator of leakage [31,34]. Evaluation of cassette leakage by several laboratories indicates that significant leakage can occur when cassettes are hand-assembled, when incorrect closing pressures are used on the cassettes and when cassettes are assembled with non-standard thicknesses of filter/backup pad combinations [34,35,36]. For press-fit cyclones, a press should be used to achieve a good seal, while screw-fit devices should have threads in good condition and be firmly screwed together.

## 5. ANALYTICAL CONSIDERATIONS

The measurement of airborne crystalline silica can be challenging. Sample preparation techniques may include complex procedures for reducing mineral interferences, redepositing the sample onto an analytical filter or using the collection filter for analysis (direct-on-filter measurement). Appropriate calibration of the analytical technique and the standard reference materials used for calibration are critical for accurate analyses. Identification of the analyte, whether quartz, cristobalite or tridymite, can be complicated by the presence of mineral interferences. There are several analytical methods to choose from, each having associated particle size effects. Thus, a high degree of attention is required throughout the analysis process. Discussion of crystalline silica measurement in bulk samples is beyond the scope of this chapter; however, a method for determining crystalline silica in bulk samples by infrared spectrometry is described elsewhere [37].

Prior to any sample preparation step, it is advisable to check the cassette received from the field for adherence of particles to the top or sides of the cassette. In an evaluation of Min-U-Sil 5 samples received in the American Industrial Hygiene Association (AIHA) Proficiency Analytical Testing (PAT) program for Rounds 146-148, it was observed that up to 20 % of the total sample was recovered by rinsing the top of the cassette prior to sample preparation [38].

Sample preparation may include procedures to reduce mineral interferences prior to analysis. A phosphoric acid digestion may be used if the presence of amorphous silica is suspected and alternate analytical peaks which are free of interferences do not provide sufficient sensitivity [39]. The phosphoric acid dissolves the amorphous silica, although some of the smaller crystalline silica particles may be lost [40]. Calcite, magnetite and hematite may be removed with dilute HCl. Kaolinite can be altered to an amorphous state through heating the sample within a specified temperature range. Some mineral interferences also may be dealt with during sample analysis via a thorough knowledge of the characteristic analytical peaks.

To ensure the accuracy of silica analysis, the sample deposit should be uniform across the filter. Since field samples are not always evenly distributed across the sampling filter, samples may be redeposited onto a different filter for analysis. The sample filter may be ashed (muffle furnace or low-temperature asher) or dissolved (tetrahydrofuran). The silica sample then is suspended in a solvent and redeposited onto an analytical filter by means of a filtration apparatus. Redeposition of the sample is difficult to perform at low sample loadings and requires the laboratory analyst to demonstrate good intralaboratory reproducibility. NIOSH and OSHA analytical methods use a 2-mL "buffer" of solvent in the filtration chimney prior to addition of the suspended sample in order to provide a cushion for more even deposition of the crystalline silica particles. No statistically significant difference in analytical results has been observed between ashing and chemical dissolution of the sample filter [40].

Direct-on-filter techniques are used by the United Kingdom, the European Union and Australia [41]. The sample collection filter is taken from the cassette and analyzed with no sample preparation. These techniques require less time and labor, avoid loss of analyte during sample preparation steps and are amenable to the predominant analytical methods [42]. Direct-on-filter methods should take into account deposition of the sample across the filter (deposition may be non-uniform) when choosing the area of the filter to measure and when comparing results to other methods. Aerosol deposits near the center of the filter are expected to be higher than deposits near edge of the filter. This potential source of error is generally minimized by using the same sampler and sampler conditions to prepare working calibration standards as was used for field sampling. Sample overloading is possible for a sample collected over a full work shift.

Calibration Standards: Calibration issues have proven to be critical in the accurate measurement of crystalline silica. Comparisons of various standard mineral reference materials used for calibration have shown varying degrees of agreement [43, 44, 45, 46]. In a statistical study of reference materials used by analytical laboratories participating in Round 133 of the PAT program, it was observed that use of multiple calibration standards contributed significantly to variability of the analytical results [40, 47]. To ensure accurate measurement of crystalline silica for analyses in the U.S., it is essential that only standard reference materials (SRMs) from the National Institute of Standards and Technology (NIST) (for which both particle size and phase purity have been established) be used to prepare calibration curves for quartz (1878 series, the current being 1878a) and cristobalite (1879 series, the current being 1879a). Efforts are being made to ensure continued availability of the NIST crystalline silica SRMs. No NIST SRM for tridymite is available, since this silica polymorph rarely exists in the workplace. However, a well-characterized sample of tridymite of the appropriate particle size is available from the U.S. Geological Survey and can be used as a reference standard. Tridymite reference material (Ref No. 210-75-0043) may be obtained from Dr. Stephen A. Wilson, U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225 (telephone: 303-236-2454; FAX 303-236-3200; e-mail: [swilson@usgs.gov](mailto:swilson@usgs.gov)).

NIST is currently producing and certifying quartz and cristobalite deposited in known amounts ( $\mu\text{g}/\text{filter}$ ) onto 25-mm PVC filters. For quartz, NIST SRM 1878a (quartz powder) deposited onto filters will be available in a "calibration set" of 6 concentration levels. NIST SRM 2950 quartz calibration set will contain 5 blank filters and 5 filters at each of the following target concentrations ( $\mu\text{g}$  quartz/filter): 10, 20, 50, 100, 250 and 500. In addition, NIST SRM 2951 will contain 5 blank filters and 5 filters at a target concentration of 5  $\mu\text{g}$  quartz/filter and NIST

SRM 2958 will contain 5 blank filters and 5 filters at a target concentration of 1000 µg quartz/filter. For cristobalite, NIST SRM 1879a (cristobalite powder) deposited onto filters will be available in a "calibration set" of 6 concentration levels. NIST SRM 2960 cristobalite calibration set will contain 5 blank filters and 5 filters at each of the following target concentrations (µg cristobalite/filter): 5, 10, 20, 50, 100 and 250. In addition, NIST SRM 2967 will contain 5 blank filters and 5 filters at a target concentration of 500 µg cristobalite/filter. These filters can facilitate preparation of routine working standards at known concentration levels. These filters may also be useful in preparation of quality assurance samples.

Industrial hygiene laboratories use a variety of analytical techniques for the quantitative determination of quartz, cristobalite and tridymite [41,48]. The three most commonly used are X-ray diffraction spectrometry (XRD), infrared absorption spectrometry (IR) and colorimetric spectrophotometry. The sensitivities of these three techniques are influenced by the sample particle size. X-ray diffraction intensity varies considerably with particle size, smaller particles (0.2 to 2.0 µm) showing lower intensities [49]. Peak broadening and extinction effects are related to particle size; there is a decrease in intensity at larger particle diameters (>25 µm) due to extinction [50-52]. In addition, the X-ray diffraction intensity is affected by the fact that smaller particles contain a lower proportion of crystalline material because the amorphous surface layer makes up a higher proportion of the total. The infrared absorption response of both quartz and cristobalite is particle size dependent [53,54]. The response increases as particle size decreases to about 1.5 µm; below about 1.5, the response decreases due the presence of an amorphous surface layer. If a sample contains an appreciable portion of amorphous silica, neither XRD nor IR is entirely adequate, and both methods should be used for accurate quantification [55]. Colorimetric methods typically include a precisely timed heating step in which phosphoric acid is used to dissolve amorphous silica. The acid digestion may result in the loss of some of the smaller crystalline silica particles [40]. Since particle size and amorphous layer affect all three techniques, matching the particle size and phase purity of calibration standards with field samples is very important to minimize analytical bias. Because NIST SRM 1878 series (the current being SRM 1878a) consists of quartz with a distribution of particle sizes that is intended to be representative of respirable particles sampled, use of a respirable dust sampler (such as the Dorr-Oliver 10-mm nylon cyclone) should provide a collected dust sample which matches the calibration curve of the SRM [56].

**TABLE 3. X-RAY DIFFRACTION SAMPLING AND ANALYTICAL METHODS FOR CRYSTALLINE SILICA.**

	NMAM 7500	OSHA ID-142	MSHA P-2	MDHS 51 /2
Silica polymorph	quartz cristobalite tridymite	quartz cristobalite	quartz cristobalite	quartz
Sampler	10-mm nylon cyclone, 1.7 L/min Higgins-Dewell cyclone, 2.2 L/min	10-mm nylon Dorr-Oliver cyclone, 1.7 L/min	10-mm nylon Dorr-Oliver cyclone, 1.7 L/min	Higgins-Dewell cyclone, 1.9 L/min
Filter	37-mm 5- $\mu$ m PVC membrane	37-mm 5- $\mu$ m PVC membrane	37-mm 5- $\mu$ m PVC membrane	25-mm 5- $\mu$ m PVC membrane
Volume	400-1000 L total dust < 2 mg	408-816 L total dust < 3 mg	400-1000 L total dust < 3 mg	$\geq$ 456 L total dust < 2 mg
Filter Preparation	RF plasma asher, muffle furnace or dissolve filter in THF	dissolve filter in THF	RF plasma asher	none
Redeposition	onto 0.45- $\mu$ m silver membrane filter	onto 0.45- $\mu$ m silver membrane filter	onto 0.45- $\mu$ m silver membrane filter	none
Drift Correction	silver internal standard	silver internal standard	silver internal standard	external standard e.g.: aluminum plate
X-ray source	Cu K $\alpha$ 40 kV, 35 mA	Cu K $\alpha$ 40 kV, 40 mA	Cu K $\alpha$ 50 kV, 35 mA	Cu K $\alpha$ 45 kV, 45 mA
Calibration	suspensions of SiO <sub>2</sub> in 2-propanol (deposited on silver membrane filter)	suspensions of SiO <sub>2</sub> in 2-propanol (deposited on silver membrane filter)	suspensions of SiO <sub>2</sub> in 2-propanol (deposited on silver membrane filter)	sampling from a generated atmosphere of standard quartz dust
Proficiency Testing	PAT	PAT	PAT	WASP
Range ( $\mu$ g quartz)	20-2000	50-160 (validation range)	20-500	50-2000
LOD ( $\mu$ g quartz)	5 (estimated)	10	5	3
Precision*	CV = 8 % @ 50-200 $\mu$ g	CV =10.6 % @ 50-160 $\mu$ g	CV = 10 % @ 20-500 $\mu$ g	CV = 5 % @ 50 $\mu$ g

- Precision is noted in terms of CV (coefficient of variation) for all methods for convenience of comparison. CV is equivalent to  $s_r$  (relative standard deviation). In some methods, precision is noted in terms of  $\bar{s}_r$  (pooled relative standard deviation) which is equivalent to  $\overline{CV}$ .  
 NMAM=NIOSH Manual of Analytical Methods, OSHA=Occupational Safety and Health Administration, MSHA=Mine Safety and Health Administration, MDHS=Methods for Determination of Hazardous Substances, PVC=polyvinyl chloride, RF=radio frequency, THF=tetrahydrofuran, Cu=copper, kV=kilovolts, mA=milliamps, PAT=proficiency analytical testing, WASP=workplace analysis scheme for proficiency, LOD=limit of detection, CV = coefficient of variation.

XRD Methods. XRD methods include NIOSH Manual of Analytical Methods (NMAM) 7500, OSHA ID-142, MSHA P-2 and UK-HSE Methods for the Determination of Hazardous Substances (MDHS) 51 /2 [57-60]. Details of these methods are listed in Table 3. X-ray diffraction is capable of distinguishing between the different polymorphs of crystalline silica: quartz, cristobalite and tridymite.

The primary diffraction line for  $\alpha$ -quartz is  $26.66^\circ 2\theta$  (3.343 Å). Since silica often occurs in a matrix with other minerals, some of which exhibit spectra that overlap with the primary quartz diffraction peak, the use of alternate peaks for quantification may be necessary. A list of potential mineral interferences is given in OSHA ID-142, Appendix A [58]. The use of secondary, tertiary and even quaternary peaks may result in decreased sensitivity [61]. An X-ray diffraction scan to characterize the environmental matrix for a set of samples is required in NIOSH X-ray diffraction methods for each set of samples. A determination revealing the correct peak ratios for the three largest peaks can be taken as an indicator of lack of interferences; otherwise a phosphoric acid digestion may be required prior to analysis to reduce interferences [39]. A high level of analyst expertise is required to optimize instrument parameters and correct for matrix interferences either during the sample preparation phase or the data analysis and interpretation phase [62]. NIOSH XRD methods suggest that XRD analysts have some training (university or short course) in crystallography or mineralogy in order to have a background in crystal structure, diffraction patterns and mineral transformation. This is important for understanding the matrix in which the sample was taken.

For optimum XRD instrument performance, the X-ray source must be aligned and monitored routinely for stability. Counting statistics, which are crucial for precise measurement of peak intensity, can be improved by increasing the count time per increment, although this increases the total time per sample analysis. The scan rate of the detector should be no more than  $1^\circ 2\theta \text{ min}^{-1}$ . Error increases rapidly with increasing scan rate. A  $1^\circ$  divergence slit width is reasonable for measurement in the  $20\text{-}80^\circ 2\theta$  range. For optimal intensity and resolution, the receiving slit width should be  $>0.2^\circ$  and about the same as the X-ray beam width. Inherent properties of the sample, such as crystallinity, can also affect measured peak intensities. Parameters related to sample preparation include sample homogeneity, size distribution of the particles, size of the sample surface exposed to the X-ray beam, thickness of the sample deposition and choice of internal standards, if any. An internal standard, such as silver in NMAM 7500 and OSHA ID-142, serves to normalize the X-ray intensity measured and to provide information on matrix absorption effects. Sample spinning during analysis allows for the alignment of each crystal in the beam and thus reduces precision error by insuring that all crystals are measured. Monitoring X-ray tube emission is done via a permanently mounted standard (e.g.; NIST SRM 1976, a sintered alumina plate used as an instrument sensitivity standard for X-ray powder diffraction). In addition, line position and line shape can be monitored via silicon powder (NIST SRM 640c) or lanthanum hexaboride powder (NIST SRM 660a). Direct-on-filter methods depend on an external standard, such as an aluminum plate to correct for the gradual decline in X-ray tube emission [60].

**TABLE 4. INFRARED SAMPLING AND ANALYTICAL METHODS FOR CRYSTALLINE SILICA.**

	NMAM 7602	NMAM 7603	MSHA P-7	MDHS 37	MDHS 38
Matrix		coal mine dust	coal mine dust		
Sampler	10-mm nylon cyclone, 1.7 L/min  Higgins-Dewell cyclone, 2.2 L/min	10-mm nylon cyclone, 1.7 L/min  Higgins-Dewell cyclone, 2.2 L/min	10-mm nylon Dorr-Oliver cyclone, 2.0 L/min	Higgins-Dewell cyclone, 1.9 L/min	Higgins-Dewell cyclone, 1.9 L/min
Filter	37-mm 0.8 PVC or 5- $\mu$ m MCE	37-mm 0.8 PVC or 5- $\mu$ m MCE	37-mm 0.8- $\mu$ m, 5- $\mu$ m PVC pre-weighed	37-mm 0.8- $\mu$ m, 5- $\mu$ m PVC	37-mm 0.8- $\mu$ m, 5- $\mu$ m PVC
Volume	400-800 L total dust < 2mg	300-1000 L total dust < 2mg	not stated	$\geq$ 456 L total dust < 1 mg	$\geq$ 456 L total dust < 0.7mg
Filter Prep	RF plasma asher or muffle furnace	RF plasma asher or muffle furnace	RF plasma asher	none	muffle furnace
Analytical Sample Prep	mix residue with KBr, press 13-mm pellet	redeposit on 0.45- $\mu$ m acrylic copolymer filter	redeposit on 0.45- $\mu$ m acrylic copolymer filter	none	mix residue with KBr, press 13-mm pellet
Standard	polystyrene film	polystyrene film	polystyrene film	polystyrene film	polystyrene film
Calibration	quartz diluted in KBr	suspensions of quartz in 2-propanol	suspensions of quartz in 2-propanol	sampling from a generated atmosphere of standard quartz dust	sampling from a generated atmosphere of standard quartz dust
Proficiency Testing	PAT	PAT	PAT	WASP	WASP
Range ( $\mu$ g quartz)	10-160	30-250	25-250	10-1000	5-700
LOD ( $\mu$ g quartz)	5 (estimated)	10 (estimated)	10	varies with particle size	varies with particle size
Precision*	CV < 15 % @ 30 $\mu$ g	CV = 9.8 % @ 100 - 500 $\mu$ g	CV = 5-10 % @ 100 - 500 $\mu$ g	CV = 5 % @ 50 $\mu$ g	CV = 5 % @ 50 $\mu$ g

- Precision is noted in terms of CV (coefficient of variation) for all methods for convenience of comparison. CV is equivalent to  $s_r$  (relative standard deviation). In some methods, precision is noted in terms of  $\overline{CV}$  (pooled relative standard deviation) which is equivalent to  $\overline{CV}$ .

NMAM=NIOSH Manual of Analytical Methods, MSHA=Mine Safety and Health Administration, MDHS=Methods for Determination of Hazardous Substances, PVC=polyvinyl chloride, MCE=methyl cellulose ester, RF=radio frequency, KBr=potassium bromide, PAT=proficiency analytical testing, WASP=workplace analysis scheme for proficiency, LOD=limit of detection, CV=coefficient of variation.

Infrared Methods. IR methods include NMAM 7602, NMAM 7603, MSHA P-7, MDHS 37 and MDHS 38 [63-67]. Details of these methods are listed in Table 4.

The different polymorphs of crystalline silica exhibit distinct absorption patterns with primary and secondary absorption lines [68]. Alpha-quartz exhibits a characteristic doublet at 798-790 and 779-780  $\text{cm}^{-1}$  and secondary peaks at 694, 512, 460, 397 and 370  $\text{cm}^{-1}$ . The 694  $\text{cm}^{-1}$  peak may be used for quantification in cases where mineral interferences overlap with the primary doublet. Alpha-quartz may be quantified in the presence of amorphous silica by using the 694  $\text{cm}^{-1}$  peak or, alternatively, a phosphoric acid digestion may be used prior to analysis. Cristobalite exhibits characteristic peaks at 798, 623, 490, 385, 297 and 274  $\text{cm}^{-1}$ . The 623  $\text{cm}^{-1}$  peak may be used for quantification in cases where mineral interferences overlap with the customarily used 798  $\text{cm}^{-1}$  peak. Tridymite exhibits characteristic peaks at 793, 617 and 476  $\text{cm}^{-1}$ . It may not be possible to quantify tridymite in the presence of alpha-quartz or cristobalite [69]. Matrix effects from interferences with other silicates (such as kaolinite) present analysis problems. There is a potential for bias when correcting for matrix absorption effects, with the bias increasing at low levels of quartz. In coal mining the assumption is made that alpha-quartz is the only polymorph present due to the geological processes involved in coal formation. The only mineral interference found in coal is kaolinite. MSHA P-7 gives a spectral correction procedure for eliminating IR interference from kaolinite [65]. Although most analytical chemists are familiar with the IR technique as applied to organic analyses, mineralogical samples require additional knowledge of geology and mineralogy to correctly interpret crystal structure, matrix interferences and mineral transformation for the laboratory client. In addition, data bases of IR spectra for minerals and inorganic compounds can be valuable resources [e.g., 70].

Colorimetric Methods. The colorimetric methods for crystalline silica [e.g., 71] are significantly less precise than either the X-ray or the infrared methods. The colorimetric analytical technique exhibits a nonlinear dependence on the mass of crystalline silica present [72]. There is a limited linear range and significant blank values (20  $\mu\text{g}$  silica or higher) are common [39,72,73]. High intralaboratory variability (up to twice as high as XRD or IR) of the colorimetric methods has been noted in studies of Proficiency Analytical Testing (PAT) program results [40]. The colorimetric method is less precise than IR or XRD methods and has no advantage over these two techniques of analysis; therefore the colorimetric methods should no longer be used for routine measurement of exposure to crystalline silica.

Quality Assurance. Because of the complex nature of crystalline silica analysis, it is essential to have a quality assurance program which incorporates strict adherence to standardized procedures. The most important requirement should be following the analytical methods exactly as written. Any modifications made in the methods in daily laboratory practices should be accompanied by validation data demonstrating equivalency of the modified method. Other factors which are important in measurement accuracy and precision and should be tracked are sample preparation, calibration and proficiency testing.

In methods which redeposit the sample onto an analytical filter, redeposition techniques can be difficult, especially for low sample loadings, and require good intralaboratory precision. For methods involving redeposition of the sample, the entire analysis is dependent upon the uniform deposition of silica material onto the analytical filter for laboratory analysis. The analyst's ability to perform this step quantitatively and repeatably should be determined initially and periodically thereafter.

The most important calibration factor is the use of prescribed reference materials (i.e., NIST-certified SRMs for analyses in the U.S.). In addition, preparation of precise working standards at appropriate concentrations for calibration graphs is crucial. An optimal calibration approach is the preparation of multiple working standards from suspensions of SRMs, with care taken that the particles are deposited onto the analytical filter in an even thin layer. Five or more standards should be used to construct calibration curves. NIOSH methods require the inclusion of several low level calibration standards (20-50 µg). Calibration should be checked each day that samples are analyzed via measurement of laboratory QC samples. The NIST-certified "calibration sets" are intended to be a resource for the preparation of working standards and laboratory QC samples. In studies of PAT laboratory performance, it was found that laboratories that did not use five or more standards, did not include low level standards (<50 µg) or did not check calibration each day that samples were analyzed were found to have poor agreement with other laboratories participating in proficiency testing [47,74]. For direct-on-filter methods, working standards are prepared by air generation in a chamber [60]. It can be difficult to generate low-level standards (< 50 µg) with precision; it is advisable to use standardized equipment to ensure that deposition of standard materials across the filter matches the deposition of the field samples being analyzed.

Internal Quality Assurance data can be used to track the precision of analyses to demonstrate repeatability of measurements. Data from proficiency testing programs, such as AIHA's Proficiency Analytical Testing (PAT) Program (U.S.) and the Health and Safety Executive's Workplace Analysis Scheme for Proficiency (WASP) Program (U.K.), can be used by the laboratory to demonstrate reproducible results when compared to other laboratories participating in that program. Proficiency testing data should not be used for assessing performance of analytical methods [75].

## 6. FEASIBILITY OF SILICA ASSESSMENT AT VARIOUS CONCENTRATIONS

The efficacy of sampling and analytical methods for measuring concentrations of hazardous materials may be established using the NIOSH accuracy criterion, requiring better than 25% accuracy at concentrations within the working range of the method [76]. Accuracy, as a percentage of true concentration values, is defined in terms of an interval expected to contain 95% of (future) measurements. To account for method uncertainty, the upper 95%-confidence limit on the accuracy is measured and used in the criterion. Generally, the accuracy of a method is measured over a range of concentrations bracketing the permissible exposure limit (PEL). Use of a range of measurements means that accuracy is assured both at levels below the PEL for possible use in action level determinations and, more significantly, at the PEL itself, where method results must be legally defensible.

NIOSH has evaluated both an XRD silica method (NIOSH Method P&CAM 259, the forerunner to NIOSH Method 7500) and an IR silica method (MSHA Method P-7) in a collaborative test among several laboratories [77]. Experimental conditions and results are summarized in Tables 5 and 6. As indicated, both XRD and IR methods fulfill the NIOSH accuracy criterion over the range of filter loadings measured.

**TABLE 5. INTRALABORATORY RESULTS FOR EVALUATION OF XRD SILICA METHOD.**

Item	Filter Loading		
	69.4 µg/filter	98.4 µg/filter	204 µg/filter
Degrees of Freedom	12	11	12
RSD for sampling and analytical methods (%)*, †	8.8	6.3	8.1

Source: NIOSH, BOM [1983].

• RSD = relative standard deviation. RSD for sampling and analytical methods represents the RSD in mass estimates, accounting for intersampler and analytical variability.

† Implications for XRD: Pooled filter levels and pump error (assumed to be <5%) indicate that the overall imprecision is as follows: Total RSD for sampling and analytical methods is 9.3 %. Therefore, the upper 95% confidence limit on the accuracy (35 degrees of freedom) is 21%.

**TABLE 6. INTRALABORATORY RESULTS FOR EVALUATION OF IR SILICA METHOD.**

Item	Filter Loading		
	67.2 µg/filter	99.7 µg/filter	161 µg/filter
Degrees of Freedom	10	12	11
RSD for sampling and analytical methods (%)*, †	5.8	7.8	7.4

Source: NIOSH, BOM [1983].

• RSD = relative standard deviation. RSD for sampling and analytical methods represents the RSD in mass estimates, accounting for intersampler and analytical variability.

† Implications for IR: Pooled filter levels and pump error (assumed to be <5%) indicate that the overall imprecision is as follows: Total RSD for sampling and analytical methods is 7.1 %. Therefore, the upper 95% confidence limit on the accuracy (33 degrees of freedom) is 17%.

The airborne concentrations of silica to which these filter loadings correspond depend on the flow rate of the pre-sampler used. Currently the Occupational Safety and Health Administration (OSHA) uses the 10-mm Dorr-Oliver nylon cyclone at a sampling rate of 1.7 L/min. The concentrations relevant to the collaborative test conditions are listed in Tables 7 and 8 and assume an 8-hour sampling period. As indicated, the traditional nylon cyclone passes the accuracy criterion over a range of concentrations bracketing 100 µg/m<sup>3</sup> (the current OSHA PEL) (see nylon cyclone data in Tables 7 and 8). In addition, since the new BGI GK2.69 cyclone (discussed in Section 4 of this chapter) is expected to conform to the ISO/CEN/ACGIH respirable aerosol sampling convention, the NIOSH accuracy criterion was applied using the 4.2 L/min sampling rate of the GK2.69 cyclone. The GK2.69 cyclone evidently is accurate over a range of concentrations bracketing 50 µg /m<sup>3</sup> (0.5 times the current OSHA PEL) (see GK2.69 cyclone data in Tables 7 and 8).

**TABLE 7. XRD METHOD EVALUATION: AIR CONCENTRATIONS ( $\mu\text{g}/\text{cm}^3$ ) CORRESPONDING TO ACTUAL FILTER LOADINGS ( $\mu\text{g}/\text{filter}$ ). [76]**

Cyclone and sampling rate	Filter loading			Applicable exposure limit
	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	
	69.4 $\mu\text{g}/\text{filter}$	98.4 $\mu\text{g}/\text{filter}$	204 $\mu\text{g}/\text{filter}$	
Nylon cyclone, 1.7 L/min	85 $\mu\text{g}/\text{m}^3$	121 $\mu\text{g}/\text{m}^3$	251 $\mu\text{g}/\text{m}^3$	100 $\mu\text{g}/\text{m}^3$
GK2.69 cyclone, 4.2 L/min	34 $\mu\text{g}/\text{m}^3$	49 $\mu\text{g}/\text{m}^3$	102 $\mu\text{g}/\text{m}^3$	50 $\mu\text{g}/\text{m}^3$

\*Eight-hour sampled masses are combined with results of NIOSH, BOM [1983].

**TABLE 8. IR METHOD EVALUATION: AIR CONCENTRATIONS ( $\mu\text{g}/\text{cm}^3$ ) CORRESPONDING TO ACTUAL FILTER LOADINGS ( $\mu\text{g}/\text{filter}$ ). [76]**

Cyclone and sampling rate	Filter loading			Applicable exposure limit
	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	$\mu\text{g}/\text{filter}$	
	67.4 $\mu\text{g}/\text{filter}$	99.7 $\mu\text{g}/\text{filter}$	161 $\mu\text{g}/\text{filter}$	
Nylon cyclone, 1,7 L/min	83 $\mu\text{g}/\text{m}^3$	123 $\mu\text{g}/\text{m}^3$	198 $\mu\text{g}/\text{m}^3$	100 $\mu\text{g}/\text{m}^3$
GK2.69 cyclone, 4.2 L/min	34 $\mu\text{g}/\text{m}^3$	50 $\mu\text{g}/\text{m}^3$	80 $\mu\text{g}/\text{m}^3$	50 $\mu\text{g}/\text{m}^3$

\*Eight-hour sampled masses are combined with results of NIOSH, BOM [1983].

## 7. SUMMARY

Silica is commonly found in the earth's crust and occurs in both crystalline and non-crystalline forms. Exposure to crystalline silica causes silicosis, is associated with pulmonary tuberculosis, lung cancer, scleroderma and may be related to autoimmune disorders and chronic renal disease.

Current methods for sampling airborne crystalline silica use a cyclone/cassette to collect the respirable fraction of the aerosol. There are several cyclones available, each with specific particle collection characteristics. To support interlaboratory precision, a single sampler which meets the ISO/CEN/ACGIH respirable sampling convention should be used.

Accurate and sensitive measurement of crystalline silica is complex. A high degree of attention is required throughout the analysis. The sample cassette should be checked for any adherence of particles to the walls of the cassette. Mineral interferences may be removed prior to analysis or may be dealt with via analytical data and a thorough knowledge of the characteristic analytical peaks. For methods involving redeposition of the sample, the entire analysis is dependent upon the uniform deposition of the particles onto the analytical filter for laboratory analysis. Calibration of the technique is crucial; the most important factors being the use of prescribed SRMs, the preparation of standards at appropriate concentrations and the use of QC samples to monitor calibration. An internal quality assurance program which incorporates strict adherence to standardized procedures is essential for measurement accuracy and precision.

Table 2 summarizes NIOSH, OSHA, MSHA, ACGIH and UK-HSE crystalline silica guidelines and limits for occupational exposure to crystalline silica. Tables 3 and 4 summarize NIOSH, OSHA, MSHA and UK-HSE sampling and analytical methods for crystalline silica. Tables 5 to 8 summarize evaluations of an XRD and an IR method.

Research on crystalline silica sampling and analysis is ongoing at NIOSH and elsewhere in government, in academia and in the private sector. Thus, this guidance is subject to revision as sampling and analytical method improvements are published.

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