

## 2 Properties, Production, and Potential for Exposure

### 2.1 Chemical and Physical Properties

In the crystalline state, one silicon atom and four oxygen atoms are arranged in an ordered, repetitive array of three-dimensional tetrahedrons. The silicon atom is the center of the tetrahedron. Each of the four corners consists of a shared oxygen atom.

Exposure to changes in temperature and pressure, either natural or synthetic, may cause the crystalline structure to change [Iler 1979; Klein and Hurlbut 1993; Navrotsky 1994; Hemley et al. 1994; IARC 1997]. An example of a naturally occurring pressure change is the transformation of alpha quartz to coesite in a rock subjected to the impact of a large meteorite [Iler 1979; Klein and Hurlbut 1993; IARC 1997]. Alpha quartz and beta quartz are the respective designations given to the low- and high-temperature crystal structures. Quartz changes from the alpha to the beta form at 573 °C (1,063 °F) [Ampian and Virta 1992; NIOSH 1983a; Virta 1993; Guthrie and Heaney 1995].

The solubility of quartz in water at room temperature ranges from 6 to 11 micrograms per cubic centimeter ( $\mu\text{g}/\text{cm}^3$ ) (6 to 11 parts per million [ppm]) as  $\text{SiO}_2$  [Coyle 1982; Iler 1979]. Quartz is slightly soluble in body fluids, where it forms silicic acid and is excreted by the urinary system [IARC 1987]. The amount of silica dissolved depends on various factors, including particle size, shape, and structure; solution temperature; viscosity; pH; the pro-

portion of dust to liquid; and the presence of trace minerals [King and McGeorge 1938; King 1937; Iler 1979; Wiecek 1988; IARC 1997; Guthrie 1997]. However, the dissolution of quartz does not contribute substantially to its clearance or to changes in its biological activity [IARC 1997; Heppleston 1984; Vigliani and Pernis 1958].

### 2.2 Number of Workers Potentially Exposed

NIOSH [1991] estimates that at least 1.7 million U.S. workers are potentially exposed to respirable crystalline silica. This estimate is based on information from the National Occupational Exposure Survey (NOES) [NIOSH 1983b] and the *County Business Patterns 1986* [Bureau of the Census 1986]. Table 1 lists the nonmining industries (excluding agriculture) and mining industries with the largest numbers of workers potentially exposed to respirable crystalline silica. In addition, an undetermined portion of the 3.7 million U.S. agricultural workers [Bureau of the Census 1997] may be exposed to dust containing a significant percentage of respirable crystalline silica [Linch et al. 1998].

### 2.3 Dust-Generating Activities, Uses, and Potential Exposures

Crystalline silica (quartz) is a component of nearly every mineral deposit [Greskevitch et al. 1992]. Thus most crystalline silica exposures are to mixed dust with variable silica content that must be measured by dust collection and

**Table 1. Nonmining and mining industries with the largest numbers of U.S. workers potentially exposed to respirable crystalline silica, 1986**

| SIC*                  | Industry   | Estimated number of workers potentially exposed (1986) <sup>†</sup> | % total workers exposed (NOES) |
|-----------------------|--|---|--------------------------------|
| Nonmining industries: |  |   |                                |
| 174                   | Masonry, stonework, tile setting, and plastering           | 131,986   | 32.7                           |
| 734                   | Services to dwellings and other buildings                  | 65,812  | 10.3                           |
| 327                   | Concrete, gypsum, and plaster products                     | 63,456  | 33.3                           |
| 176                   | Roofing and sheet metal work                               | 51,153  | 25.3                           |
| 356                   | General industrial machinery and equipment                 | 44,991  | 16.2                           |
| 807                   | Medical and dental laboratories                            | 37,063  | 30.0                           |
| 493                   | Combination of gas and electric and other utilities        | 35,074  | 21.2                           |
| 179                   | Miscellaneous special trade contractors                    | 32,615  | 7.8                            |
| 753                   | Automotive repair shops                                    | 30,826  | 7.1                            |
| 326                   | Pottery and related products                               | 29,772  | 81.7                           |
| Mining industries:    |  |   |                                |
| 13                    | Oil and gas extraction                                     | 408,175   | 100 <sup>‡</sup>               |
| 12                    | Bituminous coal and lignite mining                         | 174,131   | 100                            |
| 14                    | Mining and quarrying of nonmetallic minerals, except fuels | 100,546   | 100                            |
| 10                    | Metal mining   | 39,856  | 100                            |

Source: NIOSH [1991].

\*Standard industrial classification.

<sup>†</sup>Estimated number of workers potentially exposed to the hazards of flint, quartz, sand, or silica powder; based on data from the *County Business Patterns 1986* [Bureau of the Census 1986] and the National Occupational Exposure Survey (NOES) [NIOSH 1983b]. For SICs in which the estimates differed for individual hazards, the highest percentage was used for that SIC.

<sup>‡</sup>Exposure is assumed to be 100% in the mining industries.

analysis [Wagner 1995; Donaldson and Borm 1998].

Workers in a large variety of industries and occupations may be exposed to crystalline silica because of its widespread natural occurrence and the wide uses of the materials and products containing it. OSHA compliance officers found respirable quartz in 6,779 personal samples (8-hr TWA) taken in 255 industries that were targeted for inspection (excluding mining and agriculture). In 48% of the industries, average overall exposure exceeded the PEL for respirable quartz [Freeman and Grossman 1995]. Linch et al. [1998] applied an algorithm to OSHA compliance data from the period 1979–1995 and *County Business Patterns 1993* data [Bureau of the Census 1993] to estimate the percentage of workers by industry (excluding mining and agriculture) exposed to defined concentrations of respirable crystalline silica (e.g.,  $\geq 0.05 \text{ mg/m}^3$ ) in 1993. Area samples and samples involving complaints to OSHA were excluded from the analysis. Although data limitations could have resulted in underestimating or overestimating the number of workers exposed, the authors found 5 three-digit standardized industrial classification (SIC) codes in which an estimated number of workers were exposed to concentrations at least 10 times the NIOSH REL:

| <i>SIC</i>                               | <i>No. workers</i> |
|--|--------------------|
| 174 Masonry and plastering . . . . .     | 13,800 (1.8%)      |
| 162 Heavy construction . . . . .         | 6,300 (1.3%)       |
| 172 Painting and paper hanging . . . . . | 3,000 (1.9%)       |
| 332 Iron and steel foundries . . . . .   | 800 (0.3%)         |
| 347 Metal services . . . . .             | 400 (0.2%)         |

Additional three-digit SICs had a number of workers with crystalline silica exposures that were two or five times higher than the NIOSH REL [Linch et al. 1998].

Table 2 lists the main industries around the world in which silica exposure has been reported. Virtually any process that involves movement of earth or disturbance of silica-containing products such as masonry and concrete may expose a worker to silica (see Table 3 for uses of industrial silica sand and gravel). Table 4 presents, from selected States, the most frequently recorded occupations of U.S. residents aged 15 or above whose death certificates list silicosis as an underlying or contributory cause of death [NIOSH 1996a]. In addition, Table 5 lists published case reports of silicosis in workers from other industries and occupations.

## 2.4 Sampling and Analytical Methods

Historically, several methods have been used to measure worker exposure to airborne crystalline silica (quartz, cristobalite, or tridymite). These methods differ primarily in the analytical technique employed, although they all rely on a collection procedure that uses a cyclone for size-selective sampling. Airborne samples are collected using a cyclone to remove nonrespirable particles and an appropriate filter medium (e.g., polyvinyl chloride) to retain the respirable dust fraction. Preparation of the sample for crystalline silica determination differs depending on the type of analytical technique used. One of three analytical techniques is typically used for the quantitative determination of crystalline silica: X-ray diffraction (XRD) spectrometry, infrared absorption (IR) spectrometry, or colorimetric spectrophotometry. XRD and IR are the most common techniques used for crystalline silica analyses. The quantitative limit of detection for these methods ranges from 5 to 10  $\mu\text{g}$  per sample; but the accuracy is poor, particularly at the low filter loadings ( $\leq 30 \mu\text{g}$  per sample) that are typically collected when workplace concentrations of airborne crystalline silica are near the NIOSH REL of  $50 \mu\text{g/m}^3$  (or  $0.05 \text{ mg/m}^3$ ).

**Table 2. Main industries and activities around the world in which silica exposure has been reported**

| Industry or activity   | Operations and tasks  | Source materials   |
|--|---|--|
| Agriculture  | Plowing, harvesting, using machinery, burning agricultural waste, processing agricultural products  | Soil   |
| Mining and related milling operations  | Most occupations (underground, surface, mill) and mines (metal and nonmetal, coal), rock drilling, dredging   | Ores, associated rock  |
| Quarrying and related milling operations   | Crushing stone, sand and gravel processing, stone monument cutting and abrasive blasting, slate work (e.g., pencil manufacturing), diatomite calcination  | Sandstone, granite, flint, sand, gravel, slate, diatomaceous earth |
| Construction   | Abrasive blasting of structures and buildings, highway and tunnel construction, excavation and earth moving and digging, masonry, concrete work, demolition, dry sweeping and brushing, pressurized air blowing, jack hammering, laying railroad track, removing rust or paint, sanding and scaling, replacement of asphalt roofing, and hauling, pouring, mixing, or dumping silica-containing materials | Sand, concrete, rock, soil, mortar, plaster, shingles              |
| Glass, including fiberglass  | Raw material processing, refractory installation and repair   | Sand, crushed quartz, refractory materials                         |
| Cement   | Raw material processing   | Clay, sand, limestone, diatomaceous earth                          |
| Abrasives  | Silicon carbide production, abrasive products fabrication   | Sand, tripoli, sandstone   |
| Ceramics, including bricks, tiles, sanitary ware, porcelain, pottery, refractories, vitreous enamels | Mixing, molding, glaze or enamel spraying, finishing, sculpting, firing   | Clay, shale, flint, sand, quartzite, diatomaceous earth            |
| Iron and steel mills   | Refractory preparation and furnace repair   | Refractory material  |

(Continued)

Sources: IARC [1987; 1997], NIOSH [1979a; 1983a,b; 1996b], DOL, NIOSH [1997], Fulekar and Alam Khan [1995], Jain et al. [1977], Com [1980], Webster [1982], Froines et al. [1986], Davis [1996], Weill et al. [1994], Lucas and Salisbury [1992], Pike [1992], McCunney et al. [1987], Fairfax [1998].

**Table 2 (Continued). Main industries and activities around the world in which silica exposure has been reported**

| Industry or activity  | Operations and tasks  | Source materials   |
|---|---|--|
| Silicon and ferro-silicon foundries (ferrous and nonferrous)                    | Raw materials handling, casting, molding and shaking out, abrasive blasting, fettling, furnace installation and repair  | Sand, refractory material  |
| Metal products, including structural metal, machinery, transportation equipment | Abrasive blasting   | Sand   |
| Shipbuilding and repair   | Abrasive blasting   | Sand   |
| Rubber and plastics   | Raw materials handling  | Fillers (tripoli, diatomaceous earth)                              |
| Paint   | Raw materials handling, site preparation  | Fillers (tripoli, diatomaceous earth, silica flour)                |
| Soaps and cosmetics   | Manufacturing or occupational use of abrasive soaps and scouring powders  | Silica flour   |
| Roofing asphalt felt  | Filling and granule application   | Sand and aggregate, diatomaceous earth                             |
| Agricultural chemicals  | Raw material crushing, handling, bagging; or dumping products or raw materials  | Phosphate ores and rock  |
| Jewelry   | Cutting, grinding, polishing, buffing, etching, engraving, casting, chipping, sharpening, sculpting   | Semiprecious gems or stones, abrasives, glass                      |
| Arts, crafts, sculpture   | Pottery firing, ceramics, clay mixing, kiln repairs, abrasive blasting, sand blasting, engraving, cutting, grinding, polishing, buffing, etching, engraving, casting, chipping, sharpening, sculpting | Clays, glazes, bricks, stones, rocks, minerals, sand, silica flour |
| Dental material   | Sand blasting, polishing  | Sand, abrasives  |
| Boiler scaling  | Coal-fired boilers  | Ash and concretions  |
| Automobile repair   | Abrasive blasting, sanding, removing paint and rust   | Sand, metals, priming putty  |

**Table 3. Industrial silica sand and gravel sold or used  
by U.S. producers in 1994, by major end use**

| General use             | End use   |
|-------------------------|---|
| Sand:                   |   |
| Glass-making            | Containers, flat (plate and window), specialty, fiberglass (unground or ground)   |
| Foundry work            | Molding and core, molding and core facing (ground), refractory  |
| Metallurgical work      | Silicon carbide, flux for metal smelting  |
| Abrasive work           | Blasting, scouring cleansers (ground), sawing and sanding, chemicals (ground and unground)  |
| Fillers                 | Rubber, paints, putty, whole grain fillers/building products  |
| Ceramics                | Pottery, brick, tile  |
| Filtration              | Water (municipal, county, local), swimming pool, others   |
| Petroleum manufacturing | Hydraulic fracturing, well packing, and cementing   |
| Recreation              | Golf course, baseball, volleyball, play sands, beaches, traction (engine), roofing granules and fillers, other (ground silica or whole grain) |
| Gravel                  | Silicon, ferrosilicon, filtration, nonmetallurgical flux, other   |

Sources: IARC [1997]; BOM [1994].

**Table 4. Most frequently recorded occupations of U.S. residents aged 15 or above whose death certificates list silicosis as an underlying or contributory cause of death—selected States, 1991–1992\***

| COC <sup>†</sup> | Occupation   | Number | %                  |
|------------------|--|--------|--------------------|
| 616              | Mining machine operator                            | 39     | 16.0               |
| 889              | Laborer, except construction                       | 29     | 11.9               |
| 019              | Manager or administrator, not elsewhere classified | 11     | 4.5                |
| 633              | Supervisor or precision production occupations     | 11     | 4.5                |
| 453              | Janitor, cleaner                                   | 8      | 3.3                |
| 719              | Molding, casting machine operator                  | 8      | 3.3                |
| 243              | Supervisor or proprietor of sales occupations      | 6      | 2.5                |
| 844              | Operating engineer                                 | 6      | 2.5                |
| 637              | Machinist  | 5      | 2.1                |
| 787              | Hand molding, casting, and forming occupations     | 5      | 2.1                |
| —                | All other occupations                              | 109    | 44.9               |
| —                | Occupation not reported                            | 6      | 2.5                |
|                  | TOTAL  | 243    | 100.1 <sup>‡</sup> |

Source: NIOSH [1996a].

\*Data for 1985–1990 are reported in Table 4–11 of NIOSH [1994d].

<sup>†</sup>COC: 1980 census occupation code.

<sup>‡</sup>Column does not add to 100.0 because of rounding.

**Table 5. Other occupations\* reporting cases of silicosis in workers**

| <b>Industry or occupation</b>           | <b>Reference</b>   |
|---|--|
| Agriculture industry or forestry worker | Fennerty et al. [1983]; Dynnik et al. [1981]; Beaumont et al. [1995] |
| Brewery worker                          | Nemery et al. [1993]   |
| Confectioner                            | Canessa et al. [1990]  |
| Crystal cutter                          | Suskovic et al. [1990]   |
| Drycleaning worker                      | Seitz et al. [1982]  |
| Filter candle production worker         | Vigliani and Mottura [1948]  |
| Grave digger and well digger            | al-Kassimi et al. [1991]   |
| Kaolin worker                           | Rodriguez et al. [1985]  |
| Metal polisher                          | Malik et al. [1985]  |
| Pit digger                              | de Barros Hatem and Cavalcanti [1990]                                |
| Souvenir casting worker                 | Carel et al. [1994]  |
| Woodworker                              | Thoreux et al. [1990]  |

\*Includes only occupations not listed in Tables 2 or 4.



### 2.4.1 Sampling Methods

Current sampling methods for crystalline silica involve the use of a cyclone attached to a filter cassette to collect the respirable fraction of the airborne particulate. 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 [ISO 1991; CEN 1992; ACGIH 2001]. Also, the cyclone should exhibit sufficient conductivity to minimize the electrostatic effects on particle collection. Cyclones typically used for crystalline silica measurements include the Dorr-Oliver 10-mm nylon cyclone and the Higgins-Dewell conductive 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 are likely to occur in the workplace [Bartley et al. 1994]. The Dorr-Oliver 10-mm cyclone is required by MSHA, and the Higgins-Dewell cyclone is used in the United Kingdom. Recently, the GK2.69 cyclone [Kenny and Gussman 1997] has become 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 for better mass sensitivity. Because each type of cyclone exhibits specific particle collection characteristics, the use of a single cyclone type for each application would be advisable until evidence becomes available indicating that bias among cyclone types will not increase laboratory-to-laboratory variability.

Cyclones and filter cassettes should be leak tested to avoid gross failure in the field. 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. A micromanometer has been used to measure the pressure drop across a single type of cassette and compare it with the average pressure drop across well-sealed cassettes [Van den Heever 1994]. An alternative approach uses 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 [Baron 2001]. Measurement of cassette leakage by several laboratories indicates that significant leakage can occur in certain situations. Cassettes should be assembled using a press, and they should be routinely checked for leakage.

### 2.4.2 Analytical Methods

#### 2.4.2.1 XRD Spectrometry

XRD methods used for crystalline silica determination include NIOSH Method 7500 [NIOSH 1998], OSHA Method ID-142 [OSHA 1996], MSHA Method P-2 [MSHA 1999], and the Health and Safety Executive (HSE) Method for the Determination of Hazardous Substances (MDHS) 51/2 [HSE 1988]. Details of these methods are presented in Table 6. XRD is capable of distinguishing the three prevalent polymorphs of crystalline silica (quartz, cristobalite, and tridymite) and can simultaneously analyze for each polymorph while correcting for interferences that may be present on the sample [Madsen et al. 1995]. Although most samples collected in industrial workplaces are relatively free of mineral interferences, an XRD scan of some samples should be performed to ensure the absence of interferences through confirmation of the correct peak ratios for the three largest peaks.

**Table 6. XRD\* sampling and analytical methods for crystalline silica**

| Item                    | NIOSH<br>Method 7500  | OSHA<br>Method ID-142   | MSHA<br>Method 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                  | 400–1,000 L; total dust < 2 mg  | 408–816 L; total dust < 3 mg  | 400–1,000 L; total dust < 3 mg  | $\geq$ 456 L; total dust < 2 mg                              |
| Filter preparation      | RF plasma asher, muffle furnace, or filter dissolution in THF                       | Dissolve filter in THF  | RF plasma asher   | None   |
| Redeposition            | On 0.45- $\mu$ m silver membrane filter   | On 0.45- $\mu$ m silver membrane filter   | On 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 $K_{\alpha}$ ; 55 kV, 40 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               | $\overline{RSD}$ = 0.08<br>50–200 $\mu$ g   | $\overline{CV}$ = 0.106 @<br>50–160 $\mu$ g   | CV = 10 % @<br>20–500 $\mu$ g   | CV = 5 % @ 50 $\mu$ g  |

\*Abbreviations: Cu = copper; CV = coefficient of variation (equivalent to RSD);  $\overline{CV}$  = pooled coefficient of variation;  $K_{\alpha}$  = electron ionization energy; kV = kilovolt(s); LOD = limit of detection; mA = milliampere(s); MDHS = Methods for the Determination of Hazardous Substances (Health and Safety Executive, United Kingdom); MSHA = Mine Safety and Health Administration; NIOSH = National Institute for Occupational Safety and Health; OSHA = Occupational Safety and Health Administration; PAT = proficiency analytical testing; PVC = polyvinyl chloride; RF = radio frequency; RSD = relative standard deviation;  $\overline{RSD}$  = pooled relative standard deviation (equivalent to  $\overline{CV}$ ); THF = tetrahydrofuran; WASP = Workplace Analysis Scheme for Proficiency; XRD = X-ray diffraction.

### 2.4.2.2 IR Spectrometry

IR methods used for crystalline silica determination include NIOSH Methods 7602 and 7603 [NIOSH 1994a,c], MSHA Method P-7 [MSHA 1994], and MDHS 37 and 38 [HSE 1987, 1984]. Details of these methods are presented in Table 7. Although IR is less specific than XRD (IR methods cannot readily distinguish crystalline silica polymorphs), the technique is less expensive and can be optimized for measuring quartz in well-defined sample matrices [Madsen et al. 1995; Smith 1997; Hurst et al. 1997]. Samples that contain other silicates (such as kaolinite) and amorphous silica can present interferences in the analyses. Also, a potential for bias exists when correcting for matrix absorption effects, with an increasing risk of bias at lower quartz concentrations.

### 2.4.2.3 Colorimetric Spectrophotometry

The NIOSH colorimetric method for crystalline silica (NIOSH Method 7601) [NIOSH 1994b] is significantly less precise than IR or XRD methods. The colorimetric analytical method exhibits a nonlinear dependence on the mass of crystalline silica present [Eller et al. 1999a]. The linear range of the method is limited, and the blank values for samples can be high (20  $\mu\text{g}$  silica or higher) [Talvitie 1951, 1964; Talvitie and Hyslop 1958]. High intralaboratory variability of the method (up to twice that of IR or XRD) has been noted in studies conducted in the Proficiency Analytical Testing Program (PAT) [Shulman et al. 1992]. The colorimetric method cannot distinguish between silica and silicates, since it is based on the measurement of silicon.

### 2.4.2.4 Factors Affecting the Sensitivity and Accuracy of Analytical Techniques

Samples prepared for XRD analyses are measured directly (MDHS 51/2) or are redeposited

onto 25-mm silver membrane filters (NIOSH Method 7500 and OSHA Method ID-142). IR samples can be measured directly (MDHS 37), redeposited on an acrylic copolymer membrane filter (NIOSH Method 7603 and MSHA Method P-7), or incorporated into a potassium bromide (KBr) pellet (NIOSH Method 7602 and MDHS 38). Techniques used for redepositing the sample (both IR and XRD) are difficult to perform at low sample loadings and require the laboratory analyst to demonstrate good intralaboratory reproducibility. However, these techniques can be optimized by preparing multiple working standards from multiple suspensions of calibration standards and by ensuring that the sample is redeposited evenly as a thin layer on the filter. No statistically significant difference has been observed between ashing the filter (muffle furnace and low-temperature asher) and dissolving the filter by tetrahydrofuran before redepositing the sample [Eller et al. 1999a].

The instrument response of all three analytical techniques is influenced by the size of the particles in the sample. With XRD, the diffraction intensity (as measured by peak height) can vary considerably with particle size, with smaller particles showing lower intensities [Bhaskar et al. 1994]. The sensitivity of IR analyses decreases with increasing particle size. The colorimetric method requires the use of a precisely timed heating step with phosphoric acid to digest amorphous silica and silicates during sample preparation, causing a possible loss of some small crystalline silica particles [Eller et al. 1999a]. Since particle size affects the sensitivity of all three analytical techniques, the particle size distribution of the calibration standard should closely match the size of the particles retained on the collected sample.

For all analytical techniques, strict adherence to standardized procedures is necessary to produce accurate results. Specifically, appropriate

**Table 7. IR\* sampling and analytical methods for crystalline silica**

| Item                          | NIOSH Method 7602   | NIOSH Method 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 filter; 5- $\mu$ m PVC or MCE membrane                      | 37-mm filter; 5- $\mu$ m PVC membrane                             | 37-mm filter; 5- $\mu$ m PVC membrane, preweighed   | 37-mm filter; 5- $\mu$ m PVC membrane                        | 37-mm filter; 5- $\mu$ m PVC membrane                        |
| Volume                        | 400–800 L; total dust <2 mg                                       | 300–1,000 L; total dust <2 mg                                     | Not stated  | $\geq$ 456 L; total dust <1 mg                               | $\geq$ 456 L; total dust <0.7mg                              |
| Filter preparation            | RF plasma asher or muffle furnace                                 | RF plasma asher or muffle furnace                                 | RF plasma asher                                     | None   | Muffle furnace   |
| Analytical sample preparation | 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   | Standard suspension of quartz in 2-propanol                       | Standard suspension 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  | 10–1,000   | 5–700  |
| LOD ( $\mu$ g quartz)         | 5 (estimated)   | 10 (estimated)  | 10  | Varies with particle size                                    | Varies with particle size                                    |

See footnote at end of table.

(Continued)

**Table 7 (Continued). IR\* sampling and analytical methods for crystalline silica**

| Item      | NIOSH<br>Method 7602                    | NIOSH<br>Method 7603                          | MSHA P-7                         | MDHS 37                  | MDHS 38                  |
|-----------|---|---|----------------------------------|--------------------------|--------------------------|
| Precision | $\overline{RSD} < 0.15$<br>@ 30 $\mu$ g | $\overline{RSD} = 0.098$<br>@ 100–500 $\mu$ g | CV = 5–10 %<br>@ 100–500 $\mu$ g | CV = 5 %<br>@ 50 $\mu$ g | CV = 5 %<br>@ 50 $\mu$ g |

\*Abbreviations: CV = coefficient of variation (equivalent to RSD, relative standard deviation); IR = infrared absorption; KBr = potassium bromide; MCE = methyl cellulose ester; MDHS = Methods for the Determination of Hazardous Substances (Health and Safety Executive, United Kingdom); MSHA = Mine Safety and Health Administration; NIOSH = National Institute for Occupational Safety and Health; LOD = limit of detection; PAT = proficiency analytical testing; PVC = polyvinyl chloride; RF = radio frequency;  $\overline{RSD}$  = pooled relative standard deviation (equivalent to  $\overline{CV}$ , pooled coefficient of variation); WASP = Workplace Analysis Scheme for Proficiency.

calibration of the technique has been shown to be critical in the accurate measurement of crystalline silica [Eller et al. 1999b]. Also, it is essential that only standard reference materials from the National Institute of Standards and Technology (NIST) (for which particle size and phase purity has been established) be used to prepare calibration curves for quartz (1878a) and cristobalite (1879a) [Eller et al. 1999a]. No standard reference material 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.

Direct-on-filter techniques are used by the United Kingdom, the European Union, and Australia [Madsen et al. 1995]. These techniques require less time and labor than others and are amenable to both XRD and IR analyses [Lorberau et al. 1990]. However, direct-on-filter techniques are affected by the manner in which the particles are deposited on the filter sample (particle deposition may be nonuniform). Thus care must be taken when choosing the area of the filter to measure so that results can be compared with other methods. Sample overloading is possible for a sample collected over a full work shift.

### 2.4.3 Feasibility of Measuring Crystalline Silica at Various Concentrations

The efficacy of sampling and analytical methods for measuring concentrations of hazardous materials may be established using the NIOSH

accuracy criterion [NIOSH 1995b], which requires better than 25% accuracy at concentrations of expected method application. 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 uncertainty in method evaluations, 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 OSHA PEL. Use of a range of measurements means that accuracy is assured—both at concentrations below the PEL (for possible use in action level determinations) and, more significantly, at the PEL (where method results must be legally defensible).

NIOSH has evaluated both the XRD silica method (NIOSH Method P&CAM 259, the forerunner to NIOSH Method 7500) [NIOSH 1979b] and an IR silica method (MSHA Method P-7, equivalent to NIOSH Method 7603) in a collaborative test among several laboratories [NIOSH, BOM 1983]. One result of the test was that the accuracy of the methods was estimated by evaluating the intralaboratory variability at various filter loadings. The concentrations to which these filter loadings correspond depend on the flow rate of the pre-sampler used. Experimental conditions and results relevant to the derivation of these estimates are summarized in Tables 8 and 9. The results of the collaborative tests indicate that both the XRD and IR methods tested meet the NIOSH accuracy criterion [NIOSH 1995b] over the range of filter loadings measured. Currently, OSHA uses the 10-mm nylon cyclone at a sampling rate of 1.7 L/min for sampling crystalline silica. The concentrations relevant to the collaborative test conditions are listed in Tables 10 and 11 and assume an 8-hr sampling period. As indicated in Tables 10 and 11, the traditional nylon cyclone meets the

\*Tridymite reference material 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; Web site: <http://minerals.cr.usgs.gov/geochem>).

**Table 8. Intralaboratory results for evaluation of XRD silica method**

| Item  | Filter loading |         |        |
|---|----------------|---------|--------|
|   | 69.4 µg        | 98.4 µg | 204 µg |
| Degrees of freedom  | 12             | 11      | 12     |
| RSD for sampling and analytical methods (%) <sup>*†</sup> | 8.8            | 6.3     | 8.1    |

Source: NIOSH, BOM [1983].

<sup>\*</sup>RSD = relative standard deviation. RSD for sampling and analytical methods represents the RSD in mass estimates, accounting for intersampler and analytical variability.

<sup>†</sup>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 9. Intralaboratory results for evaluation of IR silica method**

| Item  | Filter loading |         |        |
|---|----------------|---------|--------|
|   | 67.2 µg        | 99.7 µg | 161 µg |
| Degrees of freedom  | 10             | 12      | 11     |
| RSD for sampling and analytical methods (%) <sup>*†</sup> | 5.8            | 7.8     | 7.4    |

Source: NIOSH, BOM [1983].

<sup>\*</sup>RSD = relative standard deviation. RSD for sampling and analytical methods represents the RSD in mass estimates, accounting for intersampler and analytical variability.

<sup>†</sup>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%.

**Table 10. XRD method evaluation: concentration ranges bracketing applicable exposure limits for which the NIOSH accuracy criterion is met\*  
( $\mu\text{g}/\text{m}^3$ )**

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

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

**Table 11. IR method: concentration ranges bracketing applicable exposure limits for which the NIOSH accuracy criterion is met\*  
( $\mu\text{g}/\text{m}^3$ )**

| Cyclone and sampling rate | Filter loading     |                    |                   | Applicable exposure limit |
|---------------------------|--------------------|--------------------|-------------------|---------------------------|
|                           | 6.72 $\mu\text{g}$ | 99.7 $\mu\text{g}$ | 161 $\mu\text{g}$ |                           |
| Nylon cyclone, 1.7 L/min  | 83                 | 123                | 198               | 100                       |
| GK2.69 cyclone, 4.2 L/min | 34                 | 50                 | 80                | 50                        |

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



accuracy criterion over a range of concentrations bracketing  $100 \mu\text{g}/\text{m}^3$ .

Since the GK2.69 cyclone is expected to conform to the ISO/CEN/ACGIH respirable aerosol sampling convention, the NIOSH intralab-

oratory collaborative tests can be used to establish confidence limits on its accuracy. The results of the collaborative tests indicate that the GK2.69 cyclone meets the accuracy criterion over a range of concentrations bracketing  $50 \mu\text{g}/\text{m}^3$ , as illustrated in Tables 10 and 11.