

QUARTZ AND CRISTOBALITE IN WORKPLACE ATMOSPHERES



Method Number:	ID-142
Matrix:	Air
OSHA Permissible Exposure Limits: Respirable Dust Containing Quartz:	$\text{PEL (mg/m}^3\text{)} = \frac{10 \text{ mg/m}^3}{2 + \% \text{ Respirable Quartz}}$
Respirable Dust Containing Cristobalite:	Use ½ the value calculated from the mass formula for quartz.
Collection Device:	A 5-µm pore size, 37-mm diameter polyvinyl chloride filter preceded by a 10-mm nylon Dorr-Oliver cyclone is used with a personal sampling pump.
Recommended Sampling Rate:	1.7 L/min
Recommended Air Volume:	816 L
Analytical Procedure:	A suspension of the sample particulate in tetrahydrofuran (THF) is created by dissolving the sample filter in THF and then sonicating. The sample particulate is then deposited onto a silver membrane filter and analyzed by X-ray diffraction.
Detection Limits: Qualitative:	5 µg quartz 10 µg cristobalite
Quantitative:	10 µg quartz 30 µg cristobalite
Precision and Accuracy Validation Range CV <sub>1</sub> Bias Overall Analytical Error	<u>Quartz</u> 50 to 160 µg quartz per sample 0.106 +5.2% ±26%
Method Classification:	Validated Method
Date (Date Revised):	1981 (December, 1996)

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## 1. Introduction

This method describes the collection of airborne respirable  $\alpha$ -quartz and/or cristobalite in the breathing zone of personnel and the subsequent analysis by X-ray diffraction (XRD). Tridymite can also be collected and analyzed using this method if a reference material and diffraction pattern for tridymite are used.

### 1.1 History

1.1.1 There have been several methods used to analyze quartz. These include atomic absorption, colorimetry, gravimetry, microscopy, infrared spectroscopy, and XRD. The preferred method is considered to be XRD, because it can distinguish and quantitate the different polymorphs of free silica in a widest range of industrial dust matrices.

1.1.2 The previous method (8.1) used by the OSHA Salt Lake City Technical Center (OSHA-SLTC) was an adaptation of the Talvitie method (8.2). This method could not differentiate quartz or cristobalite, and the detection limit was 50  $\mu\text{g}$ . Loss of cristobalite was also possible. To improve specificity, recoveries, and detection limits, XRD became the primary method of analysis. The X-ray method is also less tedious than the Talvitie method. This method is similar to NIOSH Method 7500 (8.3). NIOSH Method 7500 was derived from NIOSH P&CAM 259 (8.4).

### 1.2 Principle

A respirable sample is collected by drawing air at approximately 1.7 liter per minute (L/min) through a 10-mm nylon Dorr-Oliver cyclone attached to polyvinyl chloride (PVC) filter cassette. An alternative selector design to the 10-mm nylon Dorr-Oliver cyclone may be used for compliance purposes if it has been verified to achieve comparable selectivity at all five aerodynamic diameters listed in the Federal Register (8.5):

Aerodynamic diameter (unit density sphere)	Percent passing selector
2 $\mu\text{m}$	90
2.5	75
3.5	50
5.0	25
10	0

For efficient communication to distinguish the various competing models for respiratory retention, it is common to refer to only the 50% cumulative cut point in terms of the equivalent spherical aerodynamic diameter ( $D_{50}$ ). The respiratory model in the Federal Register refers to the old ACGIH definition ( $D_{50} = 3.5 \mu\text{m}$ ) which differs from both the more recent ACGIH recommended model ( $D_{50} = 4 \mu\text{m}$ ) and the BMRC model ( $D_{50} = 5 \mu\text{m}$ ). The mathematical function of each model differs the others. Adjusting the flow rate of any other sampler design until a 50% cut is achieved at 3.5  $\mu\text{m}$  aerodynamic diameter may not achieve comparable aerodynamic diameters to those specified at the 0, 25, 75, and 90% cut points. ( For a review of the various respiratory models see 8.6)

At the laboratory, the filter is dissolved in tetrahydrofuran (THF), the sample particulate is suspended in THF, and then deposited on a silver membrane. The membrane is scanned by XRD giving a series of diffraction peaks (lines) occurring at different angles relative to the sample and X-ray source. The X-ray technique is based on the Bragg equation:

$$n\lambda = 2d \sin\theta$$

where:

n is order of diffracted beam

$\lambda$  is wavelength of X-ray beam (in angstroms)

d is distance between diffracting planes (in angstroms)

$\theta$  is angle between incident X-rays and the diffracting planes (in degrees)

Note: Most X-ray spectrometers are designed to scan using degrees  $2\theta$ .

### 1.3 Advantages and Disadvantages

1.3.1 This method is specific for quartz and cristobalite; XRD can distinguish crystal structure.

1.3.2 Sample preparation is simple and analysis can be computer- controlled and automated. Also, sample preparation and analysis involves a non-destructive technique. Samples can be reanalyzed at a later date.

1.3.3 Quartz and cristobalite can be identified and quantified on three or more different angles of diffraction.

1.3.4 Interferences can be minimized by using alternate angles of diffraction, computer-assisted methods of integration, acid-washing, or wide angle scans and subsequent line matching with diffraction pattern libraries.

1.3.5 This method is more accurate and offers better sensitivity than previous methods of analysis.

1.3.6 The method is not an elemental analysis. It is highly specific; the location of diffraction peaks requires both elemental and structural parameters to be "just right". This is true for both analytes and interferences. Substitution of one element for another in a given structure results in a different diffraction line pattern. Substitution of one structure for another likewise results in a different pattern. For example, zircon ( $ZrSiO_4$ ) has a different pattern from zirconia ( $ZrO_2$ ) and indeed from any other compound containing zirconium (Zr). The diffraction pattern is therefore also independent of whether a mineralogist's chemical shorthand convention is used to describe the compound on the MSDS. For example, on an MSDS the compound zircon may be shown in mineralogist's chemical shorthand as consisting of 32.8%  $SiO_2$  and 67.2%  $ZrO_2$ . The diffraction pattern of zircon however bears no relation what-so-ever to the diffraction pattern of any mixture of the compounds  $SiO_2$  and  $ZrO_2$ . [The mineralogist's chemical shorthand is often confusing to the non-chemist, but is useful for stoichiometric information about a compound or mineral. It describes the elemental composition, oxidation states of various elements, and assumed gravimetric factors used in the chemical (elemental) analysis of the compound.]

1.3.7 A disadvantage is the high cost of instrumentation and maintenance.

1.3.8 Another disadvantage is the requirement of a known particle size distribution and a sample weight compatible with a thin-layer deposition for sample analysis.

1.4 Physical and Chemical Properties (8.7)

	$\alpha$ -Quartz	Cristobalite
CAS No.:	14808-60-7	14464-46-1
Chemical Symbol:	SiO <sub>2</sub>	SiO <sub>2</sub>
Synonyms:	free crystalline silica, silicon dioxide, silica flour	calcined diatomite
Formula Weight:	60.08	60.08
Crystalline Form:	hexagonal habit	cubic or tetragonal
Specific Gravity:	2.635-2.660	2.32
Melting Point:	1610 °C	1723 °C
Boiling Point:	2230 °C (decomposes)	2230 °C (decomposes)
Solubility:	soluble in hydrofluoric acid	soluble in hydrofluoric acid
Color:	colorless in pure form	colorless in pure form

1.5 Uses and Occupational Exposures

Quartz is primarily used as an abrasive (sandblasting, cleaning, etc.) in the production of stone, clay and glass products, and foundry molds. The most serious exposures result from quartz in the form of respirable dust produced by grinding, blasting, and mixing operations. Occupations having a high potential for exposure to quartz are listed (8.8):

Metal mining	Agriculture
Coal mining	Chemical production
Non-metallic minerals (except fuels)	Concrete work
Stone, clay, and glass products	Sandblasting
Foundries	

Cristobalite is used in the manufacture of insulation, filters, and refractory materials (8.8). In nature, cristobalite usually occurs together with tridymite. Both cristobalite and tridymite can be found naturally occurring in volcanic rock or can be synthetically produced by heating amorphous or crystalline silica. Under ideal conditions tridymite forms at temperatures above 870 °C and cristobalite above 1470 °C, however, between these temperatures (particularly in the absence of alkali or alkaline earth impurities) a disordered form of cristobalite may often form instead of tridymite (8.9.). Occupational exposure to cristobalite can occur during manufacture of stone, clay, glass, and other ceramic products. Other sources of exposure to cristobalite can occur in diatomaceous earth operations, or high temperature operations such as foundries.

2. Analytical Working Range

2.1 Qualitative detection limits for quartz are:

Diffraction Peak	Peak $\theta$ 2 $\theta$	Integration Time (s)	Detection Limit ( $\mu$ g)
Primary	26.66	1	5
Secondary	20.88	25	5
Tertiary	50.18	25	5

Note: Peak 2 $\theta$  values are dependent on instrumental characteristics and may vary slightly. The terms "peak" and "line" are used interchangeably in this method.

The detection limits listed above were determined by both parametric (t-test) and non-parametric (Rank Sum test) tests, and are stated for the 95% confidence level (8.10).

2.2 The quantitative detection limit for quartz using the primary diffraction line is 10  $\mu$ g. The coefficient of variation of 10- $\mu$ g quartz standards when using the primary line is 0.199 (8.11).

- 2.3 The qualitative and quantitative detection limit for cristobalite are 10 and 30 µg, respectively.
- 2.4 The analytical range is dependent upon the amount of interfering substances and X-ray absorbing substances present. Due to self-absorption of X rays, the upper range is also dependent on amount of sample. Total sample weights less than 3 mg are recommended. Samples with weights in excess of 3 mg can be analyzed by dividing the sample into portions and depositing onto multiple silver membranes.

### 3. Method Performance

#### 3.1 Typical quality control data over the years:

Range	80 to 200 µg quartz	50 to 160 µg quartz	50 to 210 µg quartz
CV <sub>1</sub>	0.136	0.106	0.110
Mean Recovery	95.6%	105%	96.0%
n	60	300	100
Time Period	4/1981 to 6/1981 (8.12)	12/1986 to 9/1988 (8.13)	2/1996 to 11/1996 (8.14)

Applicability of the Gaussian (normal) statistical model was tested using order statistics for the 1,000 quartz QC results (less 6 outliers) for the period from May 1987 to March 1995 and was found to be appropriate (8.15).

- 3.2 Limited data is available concerning precision and accuracy for the analysis of cristobalite; however, the sample preparation and analytical technique are the same as quartz. Analytical error should be comparable to the quartz analysis.

### 4. Interferences

According to data listed in a computer search of the Joint Committee on Powder Diffraction Studies (JCPDS) powder diffraction file (8.16), several compounds have diffraction peaks that may interfere with α-quartz or cristobalite. Such positive interferences add to the intensities of only those specific quartz diffraction peaks affected. Many of these compounds are listed in Appendix A. The majority of the interferences listed will most likely not be present together when sampling industrial operations which produce quartz or cristobalite exposures. This list is presented as line-matches found in the literature and not as definitive interferences. Exotic substances found only in research settings are not included. Even including exotic substances, α-quartz is the only substance having all four analytical diffraction peaks within ±0.20° 2θ of the theoretical angles. A substance is listed in Appendix A as a potential interference if one or more strong diffraction peaks of that substance come within ±0.65° 2θ of the specific analyte diffraction peak. Because of these broad selection criteria and the high specificity of the method for quartz, some of the listed interferences may only present a problem when a large amount of interferent is present or at temperatures other than normal laboratory conditions. The further the interference diffraction peak is from the specific analytical diffraction peak the less likely it will affect the analysis and the greater the amount (weight percentage) of interferent that can be accommodated without significant effect. The presence of interferences is actively checked for by the analyst. An interference is present in the sample when the amount of quartz or cristobalite does not agree well among the several different analytical diffraction peaks. In addition to looking for quantitative evidence of interference, the diffraction peaks are always visually inspected to see whether the peak center is shifted from that of analytical line, whether there are multiple peaks or shoulders occur in the integration range, and whether there is any unusual broadening that would indicate possible interference. Interference effects are minimized by analyzing each sample for confirmation using at least three different diffraction peaks so as to include peaks where the quartz and cristobalite results are in good agreement and where the interferent thus causes no problem. Bulk samples or a description of the process being sampled are useful in customizing a chemical cleanup procedure for any interference found difficult to resolve by software. Even so, the presence of an interference rarely jeopardizes the analysis. NIOSH Method 7500 (8.3) recommends the use of a less sensitive line when a primary interference occurs; this represents qualitative confirmation on two lines and quantitation on one line. Also mentioned in NIOSH Method 7500 is a study of samples collected in 11

different industries showing no significant interferences. Method ID-142 goes further and requires the qualitative conformation on at least three lines and quantitative confirmation on two lines. Samples results are reported as non-detected "ND" and discussed with the CSHO in those rare instances where an interference exists that cannot be resolved by software or chemical treatments. Cristobalite has fewer useful analytical diffraction peaks than quartz, is more prone to form distorted crystallites, and therefore more prone to interference problems.

- 4.1 Some elements (iron, in particular) can cause appreciable X-ray fluorescence which will result in high background intensity. This situation can be circumvented by using a diffracted beam monochromator (8.3).
- 4.2 If severe interferences are present on the primary analytical peak, results are reported using the secondary or tertiary diffraction peak. The decrease in sensitivity and precision expected when using a less sensitive line than the primary can be compensated, to a limited extent, by increasing the counting time.
- 4.3 The presence of interference can be verified and usually identified by XRD analysis. Interfering peaks are usually resolved at the OSHA-SLTC using custom in-house software (8.17) or by acid-washing the samples. Similar software developed by the instrument manufacturers or in-house can also be used.
- 4.4 Wide-angle scans are also performed to help identify interferences or assist in identification of quartz or cristobalite. These scans are usually performed with line profile libraries where the diffraction lines of the sample are compared to lines of known compounds contained in the libraries.

## 5. Sampling

### 5.1 Sampling Equipment

#### 5.1.1 Sampler assembly (if weighings are performed in the field):

- 1) Filter holder consisting of a two- or three-piece cassette, 37-mm diameter.
- 2) Backup pad, 37-mm, cellulose.
- 3) Low ash homopolymeric PVC membrane filter, 37-mm, 5- $\mu$ m pore size [part no. 625413, Mine Safety Appliances (MSA), Pittsburgh, PA or cat. no. P-503700, Omega Specialty Instrument Co., Chelmsford, MA] or equivalent.

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Note: During preparation for analysis, the sample filter is dissolved in tetrahydrofuran (THF). Certain acrylic copolymers added to PVC filters are insoluble in THF. If the membrane filter composition is unknown, a laboratory test should be conducted with THF to determine suitability before use.

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- 5.1.2 Sampler assembly (if preweighed filter cassettes are used): Cassette, Aerosol, 37-mm, Preassembled, Preweighed, LAPVC [available from Cincinnati Technical Center (CTC) OSHA Property Management Inventory System (OPMIS) or from OSHA-SLTC.]
- 5.1.3 Cyclone: Nylon, 10-mm (BDX-99R, part no. 7010048-1 Sensidyne Inc., Largo, FL, or part no. 456243, MSA, Pittsburgh, PA).
- 5.1.4 Plastic coupler for preweighed filter cassette sampling used with Cyclone Assembly: (MSA part number 457391, MSA, Pittsburgh, PA., or CTC OPMIS Filter Holding Coupler, #FES0000154).
- 5.1.5 Pump calibration system: Stop watch and bubble tube or electronic meter.
- 5.1.6 Sampling pump: Calibrate the personal sampling pump to approximately 1.7 L/min. Each pump must be calibrated with a representative sampler (cyclone, filter, etc.) in-line to minimize errors associated with uncertainties in the volume sampled. It is preferable to have a calibrated flow rate of  $1.7 \pm 0.2$  L/min, however, the literature indicates the flow rate

that gives the best estimate of the ACGIH ( $D_{50} = 3.5 \mu\text{m}$ ) respiratory model lies in the range of 1.5 to 2.0 L/min (8.18).

- 5.1.7 Assorted flexible tubing.
- 5.1.8 High volume sampling pump with cyclone (optional - for bulk sample collection).
- 5.1.9 Calibrated analytical balance (0.01 mg).
- 5.1.10 Desiccant (Drierite or similar material) and desiccating chamber if not using preweighed filters.

The last two items are not needed if the samples are weighed by the laboratory.

## 5.2 Sampling Procedure

[ Compliance safety and health officers (CSHOs) should refer to the OSHA Technical manual (8.19) for pump calibration information when sampling with cyclones.]

Samples are pre- and post-weighed on the same balance either by the industrial hygienist in the field or at the laboratory. The net sample weight provides additional information to the industrial hygienist as well as the analytical laboratory. The amount of respirable dust can be determined for the sample. In addition, other compounds having respirable dust exposure limits can be assessed and supplemental sample preparation and analysis at the laboratory may be possible if sample weights are taken. For samples weighed by the industrial hygienist:

- 5.2.1 Desiccate and then weigh the PVC filter before sampling.
- 5.2.2 Place the PVC filter and a cellulose backup pad in a two- or three-piece cassette.
- 5.2.3 Attach the cassette, which is preceded by a 10-mm nylon cyclone, to a calibrated personal sampling pump using flexible tubing.
- 5.2.4 Place the sampling assembly in the breathing zone of the worker or sampling area and place the pump in an appropriate position. Take from 408 to 816 L of air through the cassette at approximately 1.7 L/min. Do not allow the cyclone to be inverted during or after sampling. **If confirmation for cristobalite is necessary, take full shift samples if possible.**
- 5.2.5 Check the pump and sampling assembly periodically to verify performance and to monitor particulate loading on the sample filter. If the filter becomes overloaded (>3 mg) during the sampling interval, replace it with another filter.
- 5.2.6 Terminate sampling at the predetermined time and record the pump flow rate and collection time. Carefully remove the filter, desiccate, and then weigh to determine the net weight gain. Carefully replace the filter and firmly seal the cassette by placing plastic plugs in both the inlet and outlet ports.
- 5.2.7 Record on the OSHA 91 form all pertinent sample data. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the samples. Also indicate whether the requested analysis is for quartz, cristobalite or both. Operations where the material has been heated to high temperatures generally should be analyzed for both.
- 5.2.8 Identify and submit an appropriate blank filter from each lot of filters used.
- 5.2.9 Seal each filter cassette and identify it with an OSHA Form 21. Mail samples to the laboratory in a suitable container designed to prevent damage.

For samples weighed at the laboratory:

- 5.2.1a Obtain the preweighed sampling cassettes from the laboratory.
- 5.2.2a Attach the cassette, which is preceded by a 10-mm nylon cyclone, to a calibrated personal sampling pump using flexible tubing. The preweighed filter cassette is smaller than the normal 2 or 3-piece cassette and has a larger outside diameter at the inlet requiring a plastic coupler fitting for the Bendix or MSA cyclones. See 5.1.3 and 5.1.4 above.
- 5.2.3a Place the sampling assembly in the breathing zone of the worker or sampling area and place the pump in an appropriate position. Take from 408 to 816 L of air through the cassette at approximately 1.7 L/min. Do not allow the cyclone to be inverted during or after sampling. **If confirmation for cristobalite is necessary, take full shift samples if possible.**
- 5.2.4a Check the pump and sampling assembly periodically to verify performance and to monitor particulate loading on the sample filter. If the filter becomes overloaded (>3 mg) during the sampling interval, replace it with another filter.
- 5.2.5a Terminate sampling at the predetermined time and record the pump flow rate and collection time. Seal the cassette by replacing the plastic plugs in both the inlet and outlet ports.
- 5.2.6a Record on the OSHA 91 form all pertinent sample data. When other compounds are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the samples. Also indicate whether the requested analysis is for quartz, cristobalite or both. Operations where the material has been heated to high temperatures generally should be analyzed for both.
- 5.2.7a Identify and submit an appropriate blank filter from each lot of filters used.
- 5.2.8a Seal each filter cassette and identify it with an OSHA Form 21. Mail samples to the laboratory in a suitable container designed to prevent damage.

### 5.3 Bulk Samples

In order of laboratory preference, bulk samples may be one of the following:

- 1) High-volume respirable filter sample (preferably >1.0 g). Contact the SLTC for information on this.
- 2) High-volume filter sample - nonrespirable (preferably > 1.0 grams).
- 3) Representative settled dust (i.e., rafter sample (preferably > 1.0 grams).
- 4) Sample of the bulk material in the workplace (preferably 10-20 grams).

Although bulks of type 1) and 2) are the most preferred, it is recognized that 3) and 4) are often the most practical to collect. The type of bulk sample should be stated on the OSHA 91 and cross-referenced to the appropriate air sample(s).

## 6. Analysis

Samples submitted on pre-weighed filters are first submitted for gravimetric analysis. Based on the total weight gained, a determination is made whether any approach or exceed the PEL (assuming 100% crystalline silica). Those sets which might exceed PEL are resubmitted for the requested quartz and/or cristobalite analyses.



## 6.1 Safety Precautions

- 6.1.1 Tetrahydrofuran (THF) has a low flash point,  $-14\text{ }^{\circ}\text{C}$  ( $6\text{ }^{\circ}\text{F}$ ), and is extremely flammable. Always use THF in a hood. THF is an ether which can form explosive peroxides upon exposure to air; therefore, it should be stored in closed containers. Always use latex gloves, a laboratory coat, and safety glasses when handling THF. Use appropriate measures (conductive mats, wrist straps, etc.) as needed to reduce static electrical charge: electrical sparks can ignite THF vapors.
- 6.1.2 Parlodion and isopentyl acetate are flammable.
- 6.1.3 Always use a hood when grinding bulk materials or when working with dry quartz or cristobalite.
- 6.1.4 If sample acid-washing is necessary, perchloric acid ( $\text{HClO}_4$ ) is used to digest PVC filters. Perchloric acid added to organic substances can produce fires and/or explosions. If  $\text{HClO}_4$  solutions darken in color while heating, immediately remove beakers from the hotplate and carefully add a small amount of nitric acid. Only use  $\text{HClO}_4$  in exhaust hoods designed and reserved for  $\text{HClO}_4$  use.
- 6.1.5. Most X-ray diffractometers have built-in devices to prevent X-ray exposure. **These devices should not be adjusted, removed, or overridden by unauthorized individuals for any reason.**
- 6.1.6 A bench top warning light (yellow) is recommended. When lit, the warning light indicates the X-ray generator is powered up.
- 6.1.7 Most X-ray spectrometers have shutter devices which allow or prevent X rays from entering the sample chamber. **These devices should not be adjusted, removed, or overridden by unauthorized individuals for any reason.** Instrument operators should familiarize themselves with correct operation of the shutters. Sample chamber access should only be allowable when X rays from the source are completely blocked. These shutters should be routinely checked for proper operation.
- 6.1.8 If the X-ray diffractometer has a user-accessible goniometer, an additional Geiger type alarm monitor to measure the general work area is recommended. The monitor can be interfaced to the X-ray generator to provide an additional safety interlock.
- 6.1.9 Avoid inserting fingers into the sample compartment. Use forceps to change samples.
- 6.1.10 Radiation monitors are worn by all X-ray operators. These monitors consist of film badges and finger rings which are periodically analyzed to detect exposure to low-level radiation.

## 6.2 Analytical Equipment

- 6.2.1 X-ray diffractometer system consisting of:
- Automated Powder Diffractometer (APD).
  - X-ray Generator.
  - Long, fine-focus copper target X-ray tube.
  - Scintillation counter detector.
  - X-ray accessories include: pulse-height analyzer, graphite monochromator,  $2\theta$  compensating slit,  $1^{\circ}$  receiving slit, and sample spinner.
  - Recirculating cooling system for the X-ray tube.
- 6.2.2 Computer system consisting of:
- Hardware and software for data reduction and graphic presentations.

Microprocessor Interface: Between the computer and the goniometer.  
Line profile library (JCPDS-International Center for Diffraction Data Powder Diffraction File, JCPDS, Swarthmore, PA).

#### 6.2.3 Standard and sample preparation:

Centrifuge tubes: Round bottom 40-mL (Pyrex 8260).

Drying oven.

Explosion-resistant hot plate (Model HP-11515B, Sybron/Thermolyne, Dubuque, IA).

Filtration apparatus, 25 mm (Filter Holder Hydrosol Manifold, cat. no. XX25 047 00, filtering clamps, cat. no. XX10 025 03, fritted glass bases with stoppers, cat. no. XX10 025 02, and glass funnels, cat. no. XX10 025 11, Millipore Corp., Bedford, MA).

Forceps.

Latex or other THF-resistant gloves (Cat. no. 8852, American Pharmaseal Lab., Glendale, CA).

Liquid nitrogen cold-trap system for suspending media (solvent) collection (Dewar, polypropylene vacuum flask, liquid nitrogen, etc.).

Micro-analytical balance (0.01 mg) for preparing bulks.

Plastic petri dishes (Product no. 7242, Gelman Sciences, Ann Arbor, MI).

Silver membrane filters: Diameter 25-mm, 0.45- $\mu$ m pore size (Cat. no. FM25-0.45, Osmonics, Inc., Minnetonka, MN).

Teflon sheet, 0.3 to 1 mm thick.

Vacuum system.

Volumetric pipettes, eyedropper, volumetric flasks and graduated cylinders.

Ultrasonic bath.

#### 6.2.4 Bulk sample preparation for membrane deposition:

Freezer mill (Model no. 6700, Spex Industries, Edison, NJ) for plastic or other bulks that cannot be ground by a mortar and pestle.

Mortar and pestle.

Sieve or sonic sifter: Sieve, 325 mesh, (or Model ATML3P Sonic Sifter with 325 mesh sieve, ATM Corporation, Milwaukee, WI).

#### 6.2.5 Acid-washing (This equipment is only used if software is unable to resolve interferences):

All glass filtering apparatus, 47-mm (Cat. no. XX15 047 00, Millipore Corp., Bedford, MA). Phillips beakers, 125- or 250-mL.

Rotating hotplate, consisting of a variable speed and time rotator (Cat. no. R4140, American Scientific Products, McGaw Park, IL) and an electric heater, 550 W, variable rheostat (Cat. no. 61560, Precision Scientific, Chicago, IL). Adjust the heater to a differential of 70 V across the heating element and mount the heater on the rotator. Do not use this hotplate near THF or other flammable solvents.

Funnels, glass, bent-stem.

PVC filters, 0.6- $\mu$ m pore size, 47-mm diameter (Cat. no. P-064700, Omega Specialty Instrument Co., Chelmsford, MA).

### 6.3 Reagents

All chemicals should be reagent grade or better.

6.3.1 Tetrahydrofuran (THF).

6.3.2 Parlodion (Pyroxylin).

6.3.3 Isopentyl (Isoamyl) acetate.

6.3.4 Parlodion in isopentyl acetate, 1.5% (w/v): Dissolve 1.5 g of parlodion in isopentyl acetate and dilute to 100 mL with isopentyl acetate.

6.3.5 Respirable quartz (5  $\mu\text{m}$ ):

The National Institute of Standards and Technology (NIST) manufactures the standard reference material (SRM) used in the analysis of respirable quartz. NIST SRM 1878 consists of quartz in a distribution of particle sizes with a mass mean equivalent spherical diameter of 1.62  $\mu\text{m}$  that is intended to be representative of respirable particles sampled as per the respiratory model published in the Federal Register (8.20). Because XRD is generally less sensitive to the smaller crystalline particles in aerosols (8.21 and 8.22) different consensus certified quartz reference materials may be required if a new respiratory model is adopted where more of the mass may be represented by larger particles. SRM 1878 should be sieved prior to use in order to remove any particles larger than 10  $\mu\text{m}$  (8.22).

National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1878 or 1878a.

Alternative respirable quartz material (can be used if compared to one of the reference materials listed above - use appropriate gravimetric factors):

Min-U-Sil 5 Quartz (Pennsylvania Glass Sand Co., Berkley Springs, WV).

6.3.6 Respirable cristobalite: NIST SRM 1879, 1879a.

6.3.7 2-Propanol.

6.3.8 If acid-washing is necessary, the following concentrated reagents are required: Nitric acid (69-71%), perchloric acid (69-72%), phosphoric acid (85-87%), fluoboric acid (48-50%), deionized water (DI H<sub>2</sub>O), and ammonium hydroxide [(30%) aqueous ammonia].

#### 6.4 Standard Preparation

The sample preparation and analytical procedure listed below are modifications of techniques found in references 8.23-8.25.

6.4.1 Preparation of separate quartz or cristobalite stock standards:

- 1) Dry the sieved quartz (NIST SRM or equivalent material) or cristobalite for 2 h at 110 °C. This material is used for stock and working standards.
- 2) Prepare three standard suspensions in 2-propanol by first weighing 10, 50, and 200 mg of the quartz or cristobalite to the nearest 0.01 mg. Then quantitatively transfer each to individual 1-L volumetric flasks using 2-propanol, and bring each to half volume.
- 3) Disperse the analyte in the 2-propanol by using an ultrasonic bath for 10 min. Remove from the bath and allow the suspension to cool to room temperature. Dilute each flask to the mark with 2-propanol.

6.4.2 Preparation of quartz or cristobalite working standards:

- 1) Prepare a series of working standards on silver membranes from the 10-, 50-, and 200- $\mu\text{g}/\text{mL}$  stock suspensions by pipetting appropriate aliquots using the procedure outlined in step 5 below. Prepare three sets of standards for the calibration curve as shown:

Stock Standards ( $\mu\text{g/mL}$ )	Aliquot (mL)	Working Standards ( $\mu\text{g}$ )
200	5, 10, 15	1000, 2000, 3000
50	2, 5, 10	100, 250, 500
10	1, 2, 5	10*, 20*, 50

\* These standards are omitted for cristobalite analysis.

- 2) Turn on the explosion-resistant hotplate and set at the lowest setting. Place a Teflon sheet on top.
- 3) Assemble the filtering apparatus and liquid nitrogen cold trap. Connect the cold trap to the filtering apparatus to collect the waste suspending media (2-propanol or THF). The waste vapors should not enter the vacuum pump.
- 4) Center a silver membrane on a fritted-glass base of the filtering apparatus. Also center the glass chimney on top of the base and secure it with a clamp.
- 5) Add a stirring bar to the stock standard suspension and withdraw aliquots using the following technique:
  - a) Place the flask on a magnetic stirrer and turn the stirrer on until a uniform suspension is achieved.
  - b) Turn off the stirrer, remove and invert the flask, allowing the stirring bar to slide into the neck.
  - c) Shake the flask vigorously to ensure an even suspension.
  - d) Cautiously revert the flask and return it to the stirrer.
  - e) Turn on the stirrer and immediately withdraw an aliquot from the center of the stirred solution using an appropriate volumetric pipette (care should be taken not to withdraw solution above the volume mark of the pipette).
- 6) With the vacuum off, place about 2 mL of 2-propanol in the chimney of the previously assembled vacuum filtering apparatus. Transfer the pipetted aliquot to the chimney. After the transfer, bring the total volume in the chimney to 20 mL with 2-propanol.
- 7) Apply vacuum to the filtering apparatus, drawing the 2-propanol through it. This should result in a thin, even layered deposition of the analyte onto the silver membrane. Do not rinse the chimney after the material has been deposited on the membrane. Rinsing can disturb the thin layer deposition just created. Vacuum should be applied for sufficient time to dry the membrane.
- 8) Carefully disassemble the chimney and clamp. Remove the silver membrane from the fritted-glass base using forceps. Place 2 drops of 1.5% parlodion solution on a glass slide. Fix the standard to the membrane by placing the bottom side of the membrane in the parlodion solution. By capillary action, the membrane draws the parlodion solution to the analyte surface. Then place the membrane on top of the heated Teflon sheet. When thoroughly dry, place the fixed standard in a labeled Petri dish. (If placed in the plastic petri dish before dry, the membrane may become affixed to the dish.)
- 9) Inspect the deposition for uniformity; clumping indicates that insufficient sonication was used. The standard will have to be remade if a significant amount of clumping occurs.

## 6.5 Sample Preparation

- 6.5.1 When sample weights are greater than 3 mg, aliquots are taken to achieve depositions within the working range.
- 6.5.2 Examine the filter and backup pad to determine if any breakthrough to the backup pad has occurred. If there is significant breakthrough, the sample is either not analyzed or results are reported with a disclaimer (see Section 7.5.3 for reporting results).
- 6.5.3 Carefully transfer the respirable air sample (PVC filter) from the cassette to a round-bottom 40-mL centrifuge tube. Add 10 mL THF to dissolve the filter and suspend the sample. Sonicate the sample suspension for 5 to 10 min. Quantitatively transfer the suspension with rinses of THF to a glass chimney of the vacuum filtering apparatus (described in Section 6.4.2, step 3). The total volume in the chimney should not exceed 20 mL. Apply a vacuum to achieve a thin, even deposition of sample on the membrane. Do not rinse the chimney after vacuum has been applied. Remove the membrane and fix the deposition in the same manner as for a standard (Section 6.4.2, step 8).
- 6.5.4 Samples collected without a cyclone or at a flow rate outside of the range of 1.5 to 2.0 L/min should be considered as non-respirable samples (8.18). These are prepared in the same manner as respirable samples, but may not give reliable results (see Section 7.5.4 for reporting results for these samples). The particle-size distribution of non-respirable samples may not approximate the distribution of the respirable quartz or cristobalite standard material, or a uniform thin layer deposition of sample may not be possible.
- 6.5.5 To prevent the possibility of contamination, a separate filtering apparatus should be used for bulk preparation.
- 1) Bulk samples approximating respirable particle size: Weigh an aliquot of 1 to 2 mg on a PVC filter, and place in a round bottom centrifuge tube.
  - 2) Non-respirable bulks: Grind the sample to a fine powder using either a mortar and pestle or a freezer mill. Then size the sample, using a 325-mesh sieve or sonic sifter. This results in a sample particle size of less than 45  $\mu\text{m}$ . An aliquot of the sized sample is weighed on a PVC filter and then placed in a round bottom centrifuge tube.
- 6.5.6 Add THF and deposit the weighed sample onto a silver membrane in the same fashion as an air sample. Care must be taken when transferring the membrane before fixing. Fix the sample as described in Section 6.4.2, step 8.

## 6.6 Analytical Procedure

Refer to the Standard Operating Procedure (8.26) or instrument manuals for system startup and initialization procedures.

- 6.6.1 Set the X-ray generator to operate at 40 kV and 40 mA (or the maximum settings appropriate for the instrument). Using forceps, transfer a standard from the Petri dish to a sample spindle or sample holder. If using a sample spindle, secure the standard to the spindle using Vaseline or a retaining ring. Place the spindle or holder into the sample chamber. Turn on the sample spinner.
- 6.6.2 Enter the following information into the controlling unit:
1.  $2\theta$  limits for each analytical line
  2.  $2\theta$  scanning increment ( $0.02^\circ 2\theta$ )
  3. Integration and background counting times
  4. Diffraction angle calibration using the secondary silver line ( $44.33^\circ 2\theta$ )
  5. Present  $2\theta$  location of the X-ray instrument

Normal analytical parameters are:

2θ Values				
<u>Quartz</u>	<u>Scanning Range</u>	<u>Peak Location</u>	<u>Peak Range</u>	<u>D Space</u>
Primary	25.90 to 27.20	26.66	26.61 to 26.71	3.341
Secondary	20.06 to 21.40	20.88	20.83 to 20.93	4.251
Tertiary	49.40 to 50.70	50.18	50.13 to 50.23	1.817
Quaternary	59.40 to 60.70	60.00	59.95 to 60.10	1.541
<u>Cristobalite</u>	<u>Scanning Range</u>	<u>Peak Location</u>	<u>Peak Range</u>	<u>D Space</u>
Primary	21.20 to 22.50	22.00	21.95 to 22.05	4.046
Secondary	35.50 to 36.80	36.07	36.02 to 36.12	2.487
Tertiary	30.76 to 32.06	31.42	31.37 to 31.47	2.845

Note: The peak locations and d spaces listed are more informational than absolute. Peak locations are dependent on instrument and sample conditions and may vary slightly.

6.6.3 Confirm the presence of quartz or cristobalite by analyzing at least three of the lines listed above for each compound (Note: The analytical determination can end after scanning only the primary line when one of the following conditions is met:

1. The calculated exposure from the primary line analysis is less than  $0.75 \times \text{PEL}$  and the air volume is greater than 500 L.
2. The calculated exposure is less than  $0.5 \times \text{PEL}$  and the air volume is less than 500 L.

6.6.4 A two-piece calibration curve (counts vs.  $\mu\text{g}$ ) or other sigmoidal curve with forced zero intercept is recommended for the quantitation of quartz or cristobalite. The count data used are integrated counts normalized to a 1-s step. The data should be statistically weighted or transformed to best reduce the effects of observed errors of measurement on the calibration. Three practical transforms used for both the count and  $\mu\text{g}$  data include the square root, the logarithm, and the fourth root.

- a) The most common transform used in X-ray work is the square root which weights count data more equitably if Poisson counting error is the primary source of error in the measurement. The error is usually larger across the calibration range than can be accounted for by Poisson counting error alone. The additional errors arise from errors associated with taking aliquots of a suspension, particle statistics, and geometric factors in sample presentation. The square root transform of the  $\mu\text{g}$  data helps to spread the data so that it is not as tight at the low end. This helps prevent a polynomial fit from exhibiting non-monotonic behavior in the calibration range.
- b) The logarithmic transform converts the approximate geometric series of  $\mu\text{g}$  data along the abscissa into more equally-spaced data making a polynomial fit well conditioned and further preventing non-monotonic behavior. The logarithmic transform also treats the relative error in the ordinate more equitably across the calibration range. A small offset is added to each value (1 count and 1  $\mu\text{g}$ ) prior to the logarithmic transform so that zero counts and zero  $\mu\text{g}$  can be included in the calibration. The offset is removed when the inverse transform is taken.
- c) The fourth root transform is approximately intermediate in effect between the square root transform and the logarithmic transform (which is generally comparable in effect to a sixth root).

The S-shaped or sigmoidal curve is easily obtained by using a cubic polynomial on the transformed data. This shape is the consequence of several effects:

- 1) The lower region is usually expected to show reduced sensitivity due to the combined effects of:
  - i) Penetration of some of the analyte into the pores of the silver membrane which shields the analyte partially from X rays.
  - ii) Selection of narrower integration limits for less intense peaks. Wider limits would increase sensitivity at the expense of decreased precision.
- 2) The middle linear region is centered about 250 µg.
- 3) The upper region shows gradually decreasing sensitivity up to 3 mg due to sample self-absorption of X rays.

The analyst reviews the results of calibrations using the untransformed and transformed data and selects the best overall fit of the data. The corresponding transform and coefficient data are programmed into the computer interface. Calibration checks are performed during the analysis. If the curve data is not current, or analytical conditions (viewing height of sample, X-ray tube output, etc.) have changed, new curve coefficients must be generated.

6.6.5 Custom analytical computer programs are used by OSHA-SLTC to analyze samples by XRD. Further information regarding this analytical system can be found in the X-ray documentation manual (8.17) and in Appendix B. Other programs can be designed or obtained from X-ray system manufacturers.

6.6.6 Instrument considerations:

- 1) Perform a silver line calibration ( $44.33^\circ 2\theta$ ) before each standard or sample is analyzed.
- 2) Scan the standard or sample over the selected  $2\theta$  range in  $0.02^\circ$  increments.
- 3) A standard is analyzed at the start and end of a run of samples and after every fourth or fifth sample analysis to assure correct instrumental operation. A new run is defined here as beginning after any significant change in analytical condition (following power interruptions, when spikes are noted, after changing to a different set of analyte peaks, etc.).

For each sample or standard, the peak location of the secondary silver diffraction calibration line is used as an initial reference point. If the silver line intensity of a sample is much less than a standard (<40% is a suggested guideline), significant self-absorption of X rays has occurred. This is most likely due to the sample matrix and can be remedied by:

- 1) Releasing the sample from the silver membrane.
- 2) Dividing the sample into aliquots and depositing each aliquot onto a silver membrane and re-analyzing or performing the acid-wash procedure mentioned in Section 6.6.9.

6.6.7 The normal counting time for the primary quartz line is 1 s for each  $0.02^\circ$  increment. To achieve maximum sensitivity it is recommended to change counting times for the secondary and tertiary lines. These changes are dependent on the quantity of quartz found at the primary line. For a primary integrated peak sensitivity of 100 counts/µg (using a mid-range calibration standard), the recommended counting time changes in relation to microgram levels are:

Microgram level:	$\frac{>125}{1 \text{ s}}$	$\frac{>50<125}{5 \text{ s}}$	$\frac{>25<50}{10 \text{ s}}$	$\frac{<25}{25 \text{ s}}$
Counting time:				

For cristobalite, 0.02° increments and the following counting times are used:

Microgram level:	$\frac{>125}{1 \text{ s}}$	$\frac{<125}{5 \text{ s}}$
Counting time:		

Higher counting times are needed for less sensitive instrumentation.

- 6.6.8 If interferences are present in any of the primary, secondary, or tertiary lines, the analyst should evaluate different software approaches for peak area integration, an alternate analytical line, or chemical treatment to resolve the interferences. The most sensitive alternate line for quartz is listed in Section 6.6.2. This line (peak at 60.00° 2θ) may not be quantitative below 50 µg quartz. For cristobalite, the alternate lines are not very sensitive or are interference-prone.
- 6.6.9 If major, unresolvable interferences are present, the analyst should attempt to alleviate them by using the acid-wash procedure listed below. Separate samples spiked with known quantities of analyte should also be taken through this procedure to assure no loss of analyte has occurred during heating. Loss of both quartz and cristobalite has been noted during this acid-wash procedure. Losses appear to be dependent on heating temperature and particle size of the sample.
- 1) Place each sample filter (silver or PVC) into an individual 125- or 250-mL Phillips beaker. Add 5 mL of nitric acid (HNO<sub>3</sub>). If the sample is on a PVC filter, also add 2 mL perchloric acid (HClO<sub>4</sub>) (see Section 6.1.4 - do not add HClO<sub>4</sub> to silver filters).
  - 2) Place beakers on a hotplate and digest filters until approximately 1 mL remains.
  - 3) Slowly add 25 mL of phosphoric acid (H<sub>3</sub>PO<sub>4</sub>) to each beaker (if cristobalite is being analyzed, add 25 mL 1:1 H<sub>3</sub>PO<sub>4</sub>:H<sub>2</sub>O instead). Place a bent-stem glass funnel in each beaker. Then place each beaker on a rotating hotplate, allow the solution to boil, and then rotate and gently boil for 8 min.
  - 4) Remove from the hotplate, and continue to swirl until the solution reaches room temperature.
  - 5) Add 75 to 100 mL hot DI H<sub>2</sub>O while vigorously swirling each beaker.
  - 6) Wash down the sides of each beaker with 10 mL fluoboric acid (HBF<sub>4</sub>) and again vigorously swirl.
  - 7) Let each solution stand about 1 h. Filter each sample onto a PVC filter (0.6 µm) using the filtration apparatus mentioned in Section 6.2.5. Rinse the sides of the beaker with DI H<sub>2</sub>O and add the solution to the funnel assembly. Apply a vacuum.
  - 8) If excessive silver chloride or gel formation is noted on the PVC filter, add approximately 5 mL of ammonium hydroxide (aqueous ammonia) to the funnel assembly and apply a vacuum.
  - 9) Dry the PVC filter on a warm hot plate. Transfer the filter to a 40-mL centrifuge tube and proceed as in Section 6.5.3.



## 7. Calculations

As previously mentioned in Section 6.6.4, each X-ray instrument is calibrated using a curve fit. Integrated area counts versus micrograms of standard are plotted and microgram amounts of the samples are calculated for each line using this curve fit.

7.1 The PELs for quartz and cristobalite are listed on the cover page of this method (8.5).

7.2 The calculation to determine the PEL for the reportable result is:

$$\% \text{ Respirable Analyte} = \frac{\text{weight of analyte } (\mu\text{g}) \times 100}{\text{total air sample weight } (\mu\text{g})}$$

The total air sample weight (in  $\mu\text{g}$ ) is the net filter weight gain as determined by the industrial hygienist or by the laboratory. The weight of analyte is determined from the integrated analyte peak intensity obtained by XRD using the calibrated response vs. mass curve for the analyte peak.

The corresponding PELs are then calculated:

$$\text{PEL for Respirable dust containing quartz PEL (mg/m}^3\text{)} = \frac{10 \text{ mg/m}^3}{2 + \% \text{ Respirable Quartz}}$$

PEL for Respirable dust containing cristobalite (mg/m<sup>3</sup>) = Use ½ the value calculated from the mass formula for Quartz

An air concentration/PEL ratio can be determined by:

$$\text{Ratio of exposure} = \frac{\text{Air Conc}}{\text{PEL}}$$

where:

$$\text{Air Conc} = \frac{\text{total sample weight } (\mu\text{g})}{\text{total air volume (L)}}$$

Other factors may have to be considered before arriving at a final exposure value. For example, the TWA calculation may require combining two or more sample results and adjust to an 8 h work day. Consult Silicosis SEP Appendix E (8.27) or OSHA Technical Manual (8.19) or for combining sample results.

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Note: If aliquots of a sample were taken and analyzed, calculations are adjusted according to the size and number of aliquots. Results from each aliquot are combined if the sample was split into a series of aliquots. If only one aliquot was taken, the result (Analyte mg/m<sup>3</sup>) is multiplied by:

$$\frac{\text{total suspension volume}}{\text{aliquot volume taken}}$$

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7.3 If an overexposure appears to have occurred, any bulk sample(s) taken with the corresponding sample set should also be analyzed using a wide angle qualitative scan to confirm the presence of quartz or cristobalite. Bulk samples must be representative of the workplace being sampled for these scans to be meaningful. Comparisons with patterns in the powder diffraction pattern library should be made in order to match the bulk diffraction lines with quartz and/or cristobalite, and a positive identification of other compounds contained in the bulk should be attempted.

7.4 A graphic portrayal of each sample should be generated as a hard copy (for further information regarding the OSHA custom software and hard copies, see Appendix B).

## 7.5 Reporting Results

When peak limits are within acceptable ranges and analyte amounts are in agreement on at least two, preferably three lines, the reported value is taken from the most sensitive, interference-free (or interference-resolved) line.

7.5.1 Respirable air sample results for individual samples are reported to the industrial hygienist in various ways for the analytes consisting of quartz and/or cristobalite:

- a) % analyte
- b) mg respirable dust containing analyte
- c) mg respirable dust containing analyte/m<sup>3</sup>

Other laboratories may report results in various ways useful to the industrial hygienist such as mg analyte/m<sup>3</sup> so as to address various consensus standards which differ from the current PEL.

7.5.2 If the results from the analysis on the primary line indicated that the sample exposure was less than the criteria listed in Section 6.6.3, the sample result X was not subsequently confirmed on alternate lines because it did not represent a significant fraction of the PEL. The result X represents an upper estimate of the amount of quartz potentially present and is reported as:

- a) less than or equal ( $\leq$ ) X% analyte
- b)  $\leq$  or X mg analyte/m<sup>3</sup>
- c) mg respirable dust

7.5.3 Particulate present on the backup pad constitutes some sample loss. Occasionally this may be seen and can be due to a poor cassette seal on the filter, improper positioning of the filter in the cassette, or poor quality control of the filter and/or cassette. A note indicating that some of the sampled material was found on the backup pad and the reported value may be lower than actual is relayed to the compliance officer if this type of contamination occurs.

7.5.4 For samples collected without a cyclone or at a flow rate different than recommended in Section 5.1.4, results are reported as approximate % or mg/m<sup>3</sup>.

7.5.5 For bulk or high volume samples, the results are reported as approximate % quartz or cristobalite:

$$\text{Approximate \% Analyte} = \frac{\text{weight of analyte found } (\mu\text{g}) \times 100}{\text{total sample weight } (\mu\text{g})}$$

## 8. References

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#### Appendix A

##### Potential Interferences - Primary Quartz Line (Also see note below)

<u>Interferent Name, Formula</u>	<u>PDF No.</u>
Aluminum Phosphate, $AlPO_4$	10-423
Biotite, $K(Fe,Mg)_3AlSi_3O_{10}(OH)_3$	2-45
Clinoferrosilite, $FeSiO_3$	17-548
Graphite, C	23-064, 25-284, 26-1079
High albite, $NaAlSi_3O_8$	20-572
Iron carbide, $FeC$	3-411
Lead chromate, $PbCrO_4$	8-209, 38-1363, 22-385
Lead sulfate, $PbSO_4$	36-1461
Leucite, $KAlSi_2O_6$	31-967, 38-1423
Microcline, $KAlSi_3O_8$	19-932, 22-675, 22-687, 19-926
Muscovite,	
$KMgAlSi_4O_{10}(OH)_2$	21-993
$KAl_2Si_3AlO_{10}(OH)_2$	7-25
$KAl_2(Si_3Al)O_{10}(OH,F)_2$	6-263
$K(Al,V)_2(Si,Al)_4O_{10}(OH)_2$	19-814
$(K,Na)Al_2(Si,Al)_4O_{10}(OH)_2$	34-175
$(Ba,K)Al_2(Si_3AlO_{10})(OH)_2$	10-490
$(K,Ca,Na)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$	25-649
$(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$	7-42
Orthoclase,	
$KAlSi_3O_8$	31-966
$(K,Ba)(Si,Al)_4O_8$	19-3
$(K,Ba,Na)(Si,Al)_4O_8$	19-2
Potassium hydroxide, KOH	15-890
Sanidine,	
$(K,Na)AlSi_3O_8$	19-1227
$KAlSi_3O_8$	25-618
Sillimanite, $Al_2SiO_5$	38-471
Wollastonite,	
$CaSiO_3$	27-1064, 10-489, 27-88
$(Ca,Fe)SiO_3$	27-1056
Zircon, $ZrSiO_4$	6-266

##### Potential Interferences (Also see note below)

##### Secondary Quartz Line

<u>Interferent Name, Formula</u>	<u>PDF No.</u>
Aluminum Phosphate, $\text{AlPO}_4$	10-423
High albite, $\text{NaAlSi}_3\text{O}_8$	20-572
Microcline, $\text{KAlSi}_3\text{O}_8$	19-932, 22-675, 22-687, 19-926

#### Tertiary Quartz Line

<u>Interferent Name, Formula</u>	<u>PDF No.</u>
Aluminum Phosphate, $\text{AlPO}_4$	10-423
Copper, Cu	4-836

#### Primary Cristobalite Line

<u>Interferent Name, Formula</u>	<u>PDF No.</u>
Aluminum Phosphate, $\text{AlPO}_4$	11-500
High albite, $\text{NaAlSi}_3\text{O}_8$	10-393, 20-572

#### Secondary Cristobalite Line

<u>Interferent Name, Formula</u>	<u>PDF No.</u>
Aluminum Phosphate, $\text{AlPO}_4$	10-423, 11-500
High albite, $\text{NaAlSi}_3\text{O}_8$	10-393, 20-572

#### Tertiary Cristobalite Line

<u>Interferent Name, Formula</u>	<u>PDF No.</u>
Aluminum Phosphate, $\text{AlPO}_4$	11-500

PDF No. = JCPDS Powder Diffraction File Number

Note: The majority of the interferences listed above will most likely not be present when sampling industrial operations which produce quartz or cristobalite exposures. This list is presented as line-matches found in literature and not as definitive interferences. Some of these interferences may only occur when a large amount of interferent is present or at temperatures other than normal laboratory conditions. A substance is listed as a potential interference if one or more sensitive lines of that substance has a peak within  $\pm 0.65^\circ 2\theta$  of the specific analyte line.

### Appendix B

#### Graphic data portrayal and calculations - custom OSHA-SLTC programs

One of the custom OSHA-SLTC programs reads and stores diffraction count data and evaluates or presents output data in the following ways:

1. Uses a symmetric five-point digital filter (a running average with weights = 0.6, 0.8, 1.0, 0.8, 0.6) to smooth the spectral count data.
2. Identifies peaks by maximum counts.
3. Determines upper and lower  $2\theta$  integration limits.
4. Chooses the integration method (either valley to valley or perpendicular drop) by observation of background and signal counts.
5. Integrates the peak by summing counts over the selected integration range.
6. Calculates the amount of analyte in total  $\mu\text{g}$  and %.

7. Generates a hard copy report. Examples of reports used at OSHA-SLTC are shown in Figures 1 and 2.

A custom OSHA-SLTC program allows the analyst to modify the computer selection of integration limits and method for each diffraction peak. A graphic representation of the scan can be displayed and an example of a 100- $\mu$ g quartz standard is shown in Figure 1.

The analyst can choose different limit settings or change the integration method and produce a new interpretation of the data as shown in Figure 2. This scan of a sample has been re-integrated to strip an interfering peak from the primary peak integration, and an interfering shoulder has been removed from the secondary peak integration. In either Figure, areas of integration are shaded and outlying areas are non-shaded.

The abbreviation "NORM CNTS" contained within the Figures stands for normalized counts (total counts/counting time).

Other in-house or commercially available software programs are used to minimize interferences and clarify results.

Diffraction Pattern - 100 µg Quartz Standard

STANDARD

AIR VOL. • 1.00  
 SAMPLE WT. • 100. UG

AG CAL. 16305 COUNTS AT 44.30 DEG.

PRI	QTZ	SEC	QTZ	TERT	QTZ
PEAK •	26.86	PEAK •	20.86	PEAK •	38.16
LOV LIMIT •	26.28	LOV LIMIT •	20.58	LOV LIMIT •	49.62
UP LIMIT •	28.06	UP LIMIT •	21.10	UP LIMIT •	59.60
INT TIME •	1	INT TIME •	0	INT TIME •	0
NORM CNTS •	8305	NORM CNTS •	1007	NORM CNTS •	1120
EST UC •	100.7	EST UC •	100.0	EST UC •	99.9
100.6% <input type="checkbox"/>		100.6% <input type="checkbox"/>		99.9% <input type="checkbox"/>	

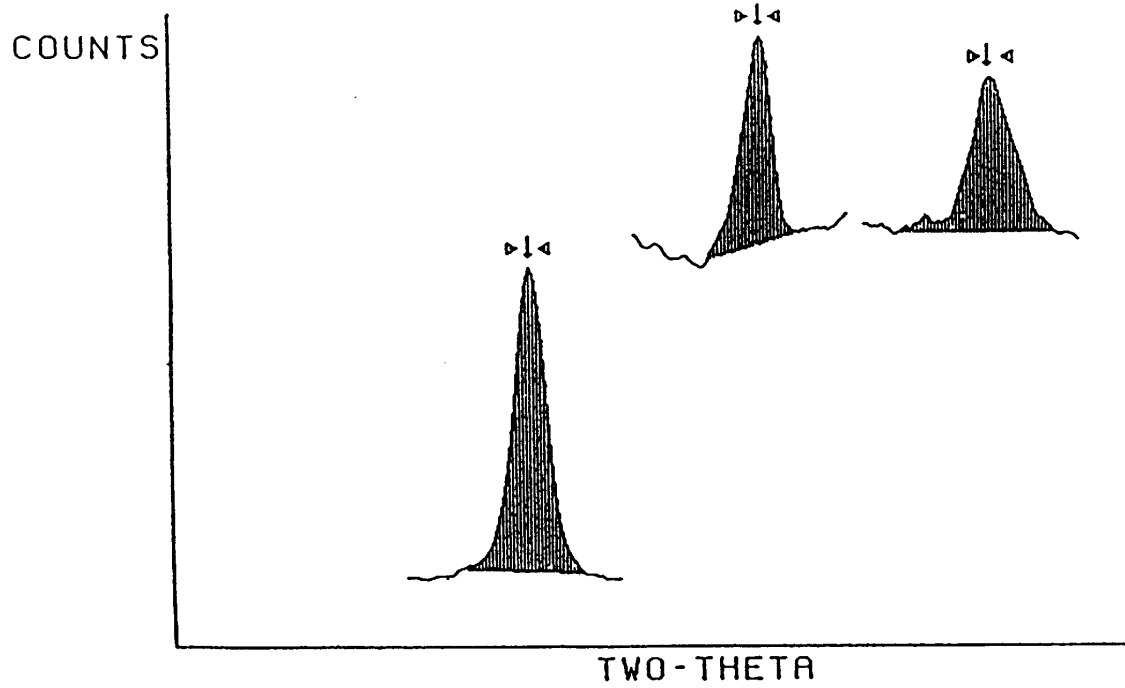


Figure 1

Quartz Diffraction Pattern - Interferences on Primary and Secondary Peaks

SAMPLE

AIR VOL. • 778.60 L  
 SAMPLE WT. • 1188. UG

AG CAL. 12120 COUNTS AT 44.31 DEG.

PRI	QTZ	SEC	QTZ	TERT	QTZ
PEAK •	28.00	PEAK •	20.90	PEAK •	50.18
LOW LIMIT •	28.20	LOW LIMIT •	20.78	LOW LIMIT •	49.90
UP LIMIT •	28.00	UP LIMIT •	21.18	UP LIMIT •	50.50
INT TIME •	1	INT TIME •	1	INT TIME •	1
NOAM CNTS •	12313	NOAM CNTS •	1827	NOAM CNTS •	1251
EST UG •	147.2	EST UG •	134.8	EST UG •	124.5
12.3 % <input type="checkbox"/>		11.3 % <input type="checkbox"/>		10.4 % <input type="checkbox"/>	

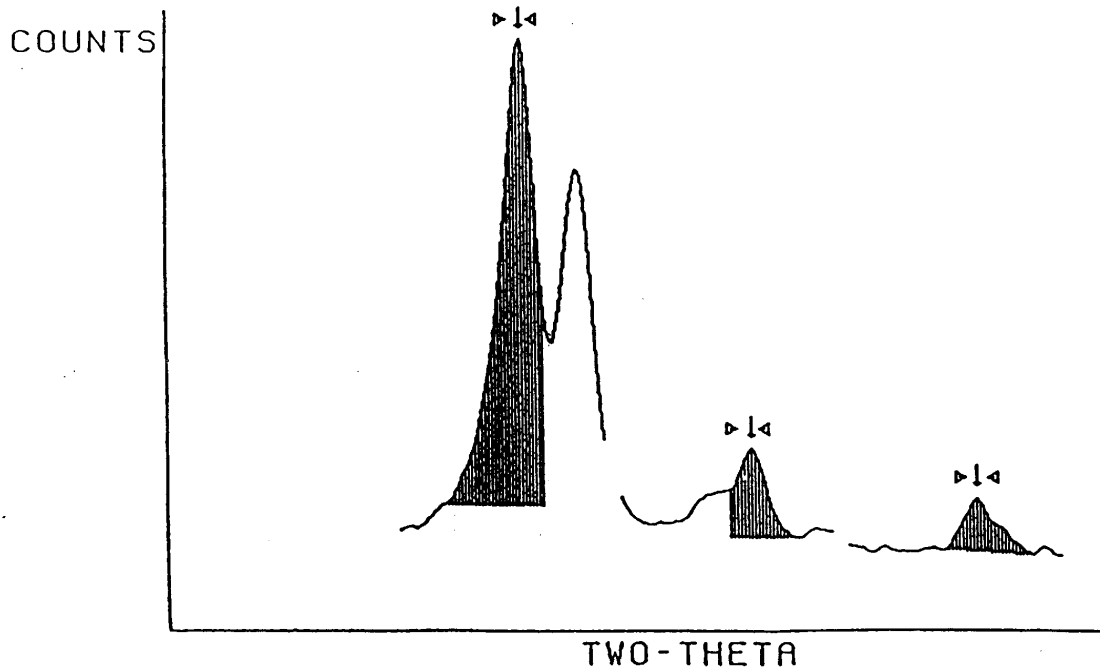


Figure 2