Crystalline Silica
Quartz and Cristobalite

Method number:	ID-142
Version:	3.0
Target concentration: (for quartz and cristobalite)	50 µg/m^3
OSHA PEL:	$\frac{10\ mg/m^3}{\%\ SiO_2 + 2}$ for quartz (mass formula) Use ½ the value calculated from the mass formula for quartz for cristobalite.
ACGIH TLV: (respirable fraction) (α-quartz and cristobalite)	0.025 mg/m^3
Procedure:	Samples are collected by drawing workplace air through pre-weighed 5-µm pore size, 37-mm diameter low ash polyvinyl chloride (PVC) filters preceded by 10-mm nylon Dorr Oliver cyclones. The weight of the respirable dust is determined by gravimetric analysis. The PVC filters are dissolved and the samples are suspended in tetrahydrofuran (THF). The samples are then deposited on silver membranes and analyzed by X-ray diffraction (XRD).
Recommended sampling time and sampling rate:	480 min at 1.7 L/min (816 L)
Reliable quantitation limit:	9.76 µg/sample (12.0 µg/m^3) quartz 20.6 µg/sample (25.2 µg/m^3) cristobalite
Standard error of estimate at the target concentration:	8.2% quartz 9.6% cristobalite
Status of method:	Fully validated method.

1981

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1. General Discussion

For assistance with accessibility problems in using figures and illustrations presented in this method, please contact the Salt Lake Technical Center (SLTC) at (801) 233-4900. These procedures were designed and tested for internal use by OSHA personnel. Mention of any company name or commercial product does not constitute endorsement by OSHA.

1.1 Background

1.1.1 History

Several analytical techniques have been used to determine crystalline silica exposure in the workplace. These techniques include atomic absorption, colorimetry, gravimetry, microscopy, infrared spectroscopy (IRS), and X-ray diffraction (XRD). OSHA Method ID-142 uses XRD which is the only technique capable of distinguishing polymorphs and quantifying crystalline silica in a wide variety of industrial dusts. This method is similar to NIOSH Method 7500.[1]

This version of OSHA Method ID-142 (version 3.0) validates analytical procedures using current OSHA method development guidelines[2] to determine accuracy, precision and overall method performance at a target concentration of 50 µg/m^3 for both quartz and cristobalite. This target concentration was chosen to match the PEL proposed by OSHA in 2013.[3] The 2013 proposal includes an action limit of 25 µg/m^3. Version 3.0 of this method incorporates the use of an auto-diluter for standard preparation, and describes the addition of carbon black to samples and standards to center the depositions in the X-ray beam. It also provides added detail for reporting data.

1.1.2 Toxic effects (This Section is for information only and should not be taken as the basis of OSHA policy.)

Two polymorphs of crystalline silica, quartz and cristobalite, have been classified as Group 1 carcinogens – "carcinogenic to humans"[4,5] by the International Agency for Research on Cancer (IARC). Health hazards associated with exposure to crystalline silica arise from the inhalation of respirable particles. Respirable crystalline silica consists of particles that are smaller than 10 µm in aerodynamic diameter.[6] In addition to causing the disabling and irreversible lung disease silicosis, respirable crystalline silica exposure also increases the risk of lung cancer,[7] renal disease,[8] and other occupational diseases including non-malignant respiratory diseases; such as chronic

[1] Key-Schwartz, R.; Ramsey, D.; Schlecht, P. Silica, Crystalline, by XRD (Filter Redeposition) (NIOSH Method 7500), 2003. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/2003-154/pdfs/7500.pdf (accessed September 2015).

[2] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed September 2015).

[3] Occupational Exposure to Respirable Crystalline Silica, Proposed Rule. Office of the Federal Register [US] Web site. https://www.federalregister.gov/articles/2013/09/12/2013-20997/occupational-exposure-to-respirable-crystalline-silica (accessed April 2015).

[4] IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. *IARC Monographs: Silica, Some Silicates, Coal Dust and Para-Aramid Fibrils* [Online]; International Agency for Research on Cancer: Lyon, FR, 2009; Vol. 68, pp 41-242. http://monographs.iarc.fr/ENG/Monographs/vol68/mono68.pdf (accessed September 2015).

[5] IARC Working Group on the Evaluation of Carcinogenic Risks to Humans. *IARC Monographs: Arsenic, Metals, Fibres, and Dusts, A Review of Human Carcinogens* [Online]; International Agency for Research on Cancer: Lyon, FR, 2009; Vol. 100 C, pp 355-406. http://monographs.iarc.fr/ENG/Monographs/vol100C/mono100C.pdf (accessed September 2015).

[6] Ziskind, M.; Jones, R. N.; Weill, H. Silicosis. *Am. Rev. Respir. Dis.* **1976,** *113*, 643-665.

[7] Liu, Y.; Steenland, K.; Rong, Y.; Hnizdo, E.; Huang, X.; Zhang, H.; Shi, T.; Sun, Y.; Wu, T.; Chen, W. Exposure-Response Analysis and Risk Assessment for Lung Cancer in Relationship to Silica Exposure: A 44-Year Cohort Study of 34,018 Workers. *Am. J. Epidemiol.* **2013,** *178*, 1424-1433.

[8] Steenland, K.; Attfield, M.; Mannejte, A. Pooled Analyses of Renal Disease Mortality and Crystalline Silica Exposure in Three Cohorts. *Ann. Occup. Hyg.* **2002,** *46*, 4-9.

obstructive pulmonary disease (COPD).[9] These occupational diseases, either alone or in concert, are life-altering and debilitating disorders.

Silicosis most commonly occurs as a diffuse nodular pulmonary fibrosis with scarring around trapped silica particles.[10] Three types of silicosis have been described: an acute form following intense exposure to respirable dust of high crystalline silica content for a relatively short period (i.e., a few months or years); an accelerated form resulting from about 5 to 15 years of heavy exposure to respirable dusts of high crystalline silica content; and, most commonly, a chronic form that typically follows less intense exposure of usually more than 20 years.[11,12]

Cristobalite was previously considered more toxic than quartz, but recent studies have shown them to have comparable pathogenic effects.[13]

1.1.3 Workplace exposure[14]

Silica minerals (SiO_2) occur in either crystalline or non-crystalline (amorphous) forms and are a component of soil, sand, and rocks. Silica minerals are sometimes called "free silica," to distinguish them from other silicates, complex mineral structures containing bound silicon dioxide. Crystalline silica is a collective term that can refer to quartz, cristobalite, tridymite, and several other rare silica minerals. The term “crystalline silica” usually refers only to the polymorphs quartz, cristobalite and tridymite. All of the crystalline silica minerals have the same chemical composition, but have different crystal structures and are thus termed polymorphs.

Quartz is the most common polymorph of crystalline silica and is the single most abundant mineral in the earth's crust.[15] During some natural and industrial processes cristobalite and tridymite are formed at high temperature from quartz, diatomaceous earth, and amorphous silica. Diatomaceous earth that has been flux-calcined (heated, usually in the presence of sodium carbonate) can contain a significant amount of cristobalite.[16]

Crystalline silica is an important industrial material, and occupational exposure can occur in a variety of workplace settings including mining, manufacturing, construction, maritime, and agriculture. Industrial processes that have been associated with high rates of silicosis include sandblasting, sand-casting foundry operations, mining, tunneling, cement cutting and demolition, masonry work, granite cutting, and hydraulic fracturing.[17] Silica flour is an extremely fine grade of silica sand that has been used as

[9] Park, R.; Rice, F.; Stayner, L.; Smith, R.; Gilbert, S.; Checkoway, H. Exposure to Crystalline Silica, Silicosis, and Lung Disease Other Than Cancer in Diatomaceous Earth Industry Workers: A Quantitative Risk Assessment. *Occup. Environ. Med.* **2002,** *59*, 36-43.

[10] Preventing Silicosis and Deaths in Construction Workers, DHHS (NIOSH) Publication No. 96-112, 1996. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/96-112 (accessed September 2015).

[11] Becklake, M. R. Pneumoconiosis. In: *Textbook of Respiratory Medicine*, Second Ed.; Murray, J. F., Nadel, J. A., Eds.; W. B. Saunders Co.: Philadelphia, PA, 1994; pp 1955-2001.

[12] Balaan, M. R.; Banks, D. E. Silicosis. In: *Environmental and Occupational Medicine*, Second Ed.; Rom, W. N., Ed.; Lippincott Williams & Wilkins: Philadelphia, PA,1992; pp 345-358.

[13] Bolsaitis, P. P.; Wallace, W. E. The Structure of Silica Surfaces in Relation to Cytotoxicity, In*: Silica and Silica-Induced Lung Diseases.* Castranova, V., Vallyathan, V., Wallace, W. E., Eds.; CRC Press, Inc.: Boca Raton, FL, 1996; pp 79-89.

[14] National Emphasis Program – Crystalline Silica, 2008. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=DIRECTIVES&p_id=3790 (accessed September 2015).

[15] Klein, C. Rocks, Minerals, and a Dusty World. *Rev. Mineral.* **1993,** *28* (Health Effects of Mineral Dusts), 8-59.

[16] Holroyd, D.; Rea, M. S.; Young, J.; Briggs, G. Health-Related Aspects of Devitrification of Aluminosilicate Refractory Fibres During Use as a High-Temperature Furnace Insulant. *Ann. Occup. Hyg*. **1988,** *32*, 171-178.

[17] Esswein, E. J.; Breitenstein, M.; Snawder, J.; Kiefer, M.; Sieber, WK. Occupational Exposures to Respirable Crystalline Silica During Hydraulic Fracturing. *J. Occup. Environ. Hyg*. **2013**, *10*, 347–356.

abrasive cleaners and inert fillers. It is also used in toothpaste, paints, rubber, paper, plastics, cements, road surfacing materials, foundry applications, and porcelain.[18]

In 2013, OSHA estimated that more than 1.8 million U.S. employees in the construction industry were exposed to silica, and 216,000 of these were exposed to concentrations greater than or equal to 250 µg/m^3. When general industry and maritime occupations were included, the numbers increased to 2.1 million exposed employees, with almost 265,000 exposed to high concentrations (≥250 µg/m^3).[19]

Most workplace exposure to crystalline silica is to quartz and to a lesser extent, cristobalite.[20] Tridymite, which is less common, is not addressed in this method because a standard reference material is not readily available.

1.1.4 Physical properties and other descriptive information[21,22]

quartz[23]

synonyms:	SiO_2; silicon dioxide; crystalline silica; α-quartz; alpha-quartz; agate; flint; chert; jasper; quartzite; chalcedony; amethyst; citrine; milky quartz; smoky quartz; rose quartz; rock crystal and many trade names
IMIS[24,25]:	9010 (respirable fraction) S103 (quartz total)
CAS number:	14808-60-7
boiling point:	2477 °C (4490 °F)
melting range:	1705 °C (3101 °F)
density:	2.6 calculated
molecular weight:	60.08
appearance:	colorless, white, yellow, gray, black, red, pink, violet, green, and many other colors based upon trace elements or particulate inclusions
molecular formula:	SiO_2
solubility:	insoluble in water; soluble in hydrofluoric acid
structural integrity:	under atmospheric pressure, converts from α-quartz to β-quartz above 573 °C; converts to tridymite above 870 °C; converts to cristobalite above 1470 °C

[18] Silica Flour: Silicosis (Crystalline Silica), DHHS (NIOSH) Publication No. 81-137, 1981. Center for Disease Control, The National Institute for Occupational Safety and Health (NIOSH) Web site. http://www.cdc.gov/niosh/docs/81-137 (accessed September 2015).

[19] Preliminary Economic Analysis and Initial Regulatory Flexibility Analysis: Supporting Document for the Notice of Proposed Rulemaking for Occupational Exposure to Crystalline Silica, 2013. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/silica/Silica_PEA.pdf (accessed September 2015).

[20] Becklake, M. R. Pneumoconiosis. In: *Textbook of Respiratory Medicine*, Second Ed.; Murray, J. F., Nadel, J. A., Eds.; W. B. Saunders Co.: Philadelphia, PA, 1994; pp 1955-2001.

[21] Amir A. C. The Quartz Page. http://www.quartzpage.de/gen_mod.html (accessed September 2015).

[22] Pough, F. H. *Rocks and Minerals,* Fifth Ed.; Houghton Mifflin: New York, 1995; pp 270-276.

[23] Anthony, J. W.; Bideaux, R. A.; Bladh, K. W.; Nichols, M. C. *Handbook of Mineralogy: Silica, Silicates*; Mineral Data Publishing: Tucson, AZ, 1995; Vol. 2, Parts 2, pp 672.

[24] Silica, Crystalline Quartz (Respirable Fraction) (Chemical Sampling Information), 2012. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/chemicalsampling/data/CH_266740.html (accessed September 2015).

[25] Silica, (Quartz Total) (Chemical Sampling Information), 2012. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/chemicalsampling/data/CH_266860.html (accessed September 2015).

cristobalite[26]

synonyms:	SiO_2; silicon dioxide
IMIS[27,28]:	9015 (silica, crystalline cristobalite, respirable dust) S105 (cristobalite total)
CAS number:	14464-46-1
boiling point:	2477 °C (4490 °F)
melting range:	1705 °C (3101 °F)
density:	2.33 calculated
molecular weight:	60.08
appearance:	colorless to off-white crystals
molecular formula:	SiO_2
solubility:	insoluble in water; soluble in hydrofluoric acid
structural integrity:	under atmospheric pressure, crystallizes from SiO_2 above 1470 °C; inverts from β-cristobalite to α-cristobalite at 268 °C or below

[26] Anthony, J. W.; Bideaux, R. A.; Bladh, K. W.; Nichols, M. C. *Handbook of Mineralogy: Silica, Silicates*; Mineral Data Publishing: Tucson, AZ, 1995; Vol. 2, Parts 1, pp 165.

[27] Silica, Crystalline Cristobalite, Respirable Dust (Chemical Sampling Information), 2012. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/chemicalsampling/data/CH_266720.html (accessed September 2015).

[28] Silica, (Cristobalite Total) (Chemical Sampling Information), 2015. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/chemicalsampling/data/CH_277225.html (accessed September 2015).

Where applicable, this method follows validation protocols drawing from the OSHA SLTC "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis".[29] These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. The unique nature of silica and its analysis prevented strict adherence to these guidelines.

2. Sampling Procedure

2.1 Apparatus

Samples are collected with pre-weighed 37-mm diameter low ash polyvinyl chloride (PVC) filters with a 5-µm pore size. OSHA uses filters contained in a custom filter cassette that is currently obtained from Zefon International Air Sampling Equipment and Medical products, part number 10012901, or equivalent. Each PVC filter is housed in an assembly composed of an aluminum cowl and a stainless steel support ring. The assembly is encapsulated in a plastic cassette.

Respirable samples are collected on a PVC filter preceded by a cyclone. When operated at experimentally determined sampling rates, cyclones are capable of sampling only those size fractions of particulates that are considered respirable with minimal bias. OSHA uses the 10-mm nylon Dorr-Oliver cyclone. Figure 2.1 shows the filter cassette and cyclone.

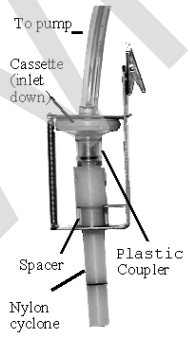

Figure 2.1. Sampling filter cassette and Dorr-Oliver cyclone.

Samples are collected using a personal sampling pump at the recommended sampling rate, calibrated with a representative sampler in-line following the procedure described in the OSHA Technical Manual.[30] The recommended sampling rate is 1.7 L/min. Do not calibrate the sampling pump with the actual filter intended to be used for compliance sampling. Samples collected using other sampling rates are considered non-respirable because the particle size fractions do not conform to the specified definition.[31]

2.2 Reagents

None required.

2.3 Technique

Assemble the sampler as shown in Figure 2.1.

Draw air directly into the inlet of the cyclone and through the filter cassette (inlet side down). The air should not pass through any hose or tubing before entering the cyclone.

Do not invert the sampler. Instruct the person being sampled not to invert the sampler. **Inverting the cyclone can cause oversize material from the cyclone grit pot to spill onto the filter**. After sampling for the appropriate time, disconnect the sampler from the sampling pump and seal the filter cassette with end plugs. Seal the sampler with a Form OSHA-21.

Submit at least one blank sample with each set of samples. Handle the blank sample in the same manner as the other samples except draw no air through it.

[29] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed September 2015).

[30] OSHA Technical Manual (OTM). United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/osta/otm/otm_ii/otm_ii_1.html#appendix_II_6 (accessed September 2015).

[31] Ettinger, H. J.; Partridge, J. E.; Royer, G. W. Calibration of Two-Stage Air Samplers. *Am. Ind. Hyg. Assoc. J,* **1970,** *31*, 537-545.

Record sample air volume (L), sampling time (min), and sampling rate (L/min) for each sample, along with any potential interferences on the Form OSHA-91A. Appendix B, Analytical Interferences, can be consulted for potential interferences.

Bulk sampling is optional. In cases where bulk samples are submitted, any of the following are acceptable in decreasing order of preference:

1) High-volume filter sample without cyclone (preferably >1.0 g). This is an air sample taken without a cyclone using a sampling rate greater than that which is recommended. This results in the sampling of a larger air volume. It is submitted and identified for analysis as a bulk sample.
2) Representative settled dust (e.g., rafter sample). Submit 1-20 grams of bulk sample in a 20-mL glass scintillation vial sealed with a PTFE-lined cap.
3) Sample of the bulk material in the workplace. Submit 10-20 grams of bulk sample in a 20-mL glass scintillation vial sealed with a PTFE-lined cap.

If bulk samples are taken, seal the sample with a Form OSHA-21. Identify the composition of the sample (if known) on a Form OSHA-91A and identify the air samples which are associated with the bulk sample(s). Ship bulk samples separately from air samples. Bulk samples can be used to confirm the presence of crystalline silica at the worksite. Bulks cannot be used to determine the exposure to respirable crystalline silica.

2.4 Recommended sampling time and sampling rate

A respirable time weighted average (TWA) sample is collected by drawing air at 1.7 liters per minute (L/min) for 480 minutes through a 10-mm nylon Dorr-Oliver cyclone attached to pre-weighed 37-mm low ash PVC filter cassette. Available research shows that this cyclone and sampling rate combination demonstrate reasonable agreement to the size selection criteria found in the Code of Federal Regulations.[32] The size selection criteria from the Code of Federal Regulations are summarized in Table 2.4.[33] An alternative selector design may be used if it has been verified to achieve comparable selectivity at all five aerodynamic diameters listed.

Table 2.4

aerodynamic diameter (unit density sphere) (µm)	percent passing selector (%)
2.0	90
2.5	75
3.5	50
5.0	25
10	0

For efficient communication, to compare particle size fraction retention of different mathematical models, it is common to refer to only the 50% cumulative cut point in terms of the equivalent spherical aerodynamic diameter. For the respiratory model used here, the 50% cumulative cut point is 3.5 µm. Adjusting the sampling rate of any other sampler design until a 50% cut is achieved at 3.5 µm aerodynamic diameter may not achieve comparable aerodynamic diameters to those specified at the 0, 25, 75, and 90% cut points.

[32] Ettinger, H. J.; Partridge, J. E.; Royer, G. W. Calibration of Two-Stage Air Samplers. *Am. Ind. Hyg. Assoc. J,* **1970,** *31*, 537-545.
[33] Table Z-3 Mineral Dusts. *Code of Federal Regulations*, Part 1910.1000, Title 29, 2001.

2.5 Interferences (sampling)

Incorrect positioning of the sampling apparatus can interfere with sampling. The cyclone must be mounted vertically. The grit pot must not become overloaded and the cyclone inlet must remain unobscured throughout the sampling time.

3. Analytical Procedure

3.1 Apparatus

An X-ray diffractometer system. A Rigaku DMAX 2500 Diffractometer equipped with a rotating anode, a copper X-ray source, and a scintillation counter detector was used in this validation. In addition to the DMAX 2000/PC Software (Ver 2.2.x.x~) used for instrument control, SLTC also uses software developed in house to calculate calibration curves and process data.

Filtering apparatus. A Millipore Corp. 6-place stainless steel Membrane Holder Manifold, catalog no. XX2504700; equipped with Glass Microanalysis Membrane Holders (for 25-mm membranes).

Glass funnels with matching fritted-glass bases. Millipore Corp. glass funnels (catalog no. XX1002514) and Millipore Corp. fritted-glass bases (catalog no. XX1002502) were used in this validation. Funnels and bases were measured and matched.

Silver membranes. SKC Inc. 0.45-µm pore size 25-mm (catalog no. 225-1803) silver membranes were used in this validation.

PVC filters. SKC Inc. 5-µm pore size 37-mm (catalog no. 225-8-01) PVC filters were used in this validation.

Micro-analytical balance (0.001 mg). A Mettler-Toledo, Inc. Model MX5 balance was used in this validation.

Auto-dilutor/dispenser. A Hamilton microLAB 600 series dilutor was used in this validation.

Hot plate. A Thermolyne Model 560G explosion-proof hotplate was used in this validation.

Ultrasonic bath. A Branson Ultrasonics Corporation Model 5510 ultrasonic cleaner was used in this validation.

Vortex mixer. A VWR International Vortex Genie 2 vortex mixer was used in this validation.

Freezer mill for bulk samples that cannot be ground with a mortar and pestle. A Spex CertiPrep Model 6770 freezer mill was used for this validation.

Microscope. A Heerbrugg Wild M3 capable of magnifying 320 to 800 times was used in this validation.

Sieve. A 325 mesh (44 micron) sieve manufactured by Dual Manufacturing Company was used in this validation.

Vacuum system equipped with a liquid nitrogen cold trap for filtering apparatus.

Centrifuge tubes, glass round bottom 50-mL, with rack to hold tubes.

Volumetric flasks, Class A, 100 and 200-mL sizes.

Erlenmeyer flasks, 250-mL with ground glass stoppers.

Glass mirror (approximately 3 × 5 inches) for fixing samples with parlodion.

Petri dishes (plastic, approximately 50-mm diameter).

PTFE sheet, 0.3 to 1 mm thick.

Dropping bottles with eyedroppers, for parlodion solution and carbon black suspension.

Dispenser bottles, 10-mL, for tetrahydrofuran (THF).

Mortar and pestle.

Laboratory metal ware, tweezers, microspatula, and single-edge razor blades.

Laboratory towels.

3.2 Reagents

All reagents should be reagent grade or better.

Quartz, [CAS no. 14808-60-7]. The quartz used in this validation was NIST Standard Reference Material (SRM) 1878a. NIST SRM 1878a is respirable quartz crushed and jet-milled to a median particle size of 1.6 µm and has a certified mass fraction purity of 93.7% ± 0.21%. When not in use, the unused portion of this material should be tightly capped in the original bottle and stored in a desiccator.

Cristobalite, [CAS no. 14464-46-1]. The cristobalite used in this validation was NIST Standard Reference Material (SRM) 1879a. NIST SRM 1879a is respirable cristobalite crushed and jet milled to a median particle size of 3.5 µm and has a certified mass fraction purity of 88.2% ± 0.4%. When not in use, the unused portion of this material should be tightly capped in the original bottle and stored in a desiccator.

2-Propanol (IPA), [CAS no. 67-63-0]. The 2-propanol used in this validation was ≥99.5% pure (lot no. SHBD6403V) purchased from Aldrich Chemical.

Parlodion, [CAS no. 9004-70-0]. The parlodion (pyroxylin) used in this validation (lot no. CBJC) was purchased from Mallinckrodt.

Isopentyl acetate, [CAS no. 123-92-2]. The isopentyl acetate used in this validation was ≥99% pure (lot no. 06714HCX) purchased from Aldrich Chemical.

Tetrahydrofuran (THF), [CAS no. 109-99-9]. The THF used in this validation was ≥99% pure and inhibited with 250 ppm BHT (lot no. SHBF4742V) purchased from Sigma-Aldrich Chemical.

Carbon black, [CAS no. 1333-86-4]. The carbon black used in this validation (lot no. 061965) was purchased from Fisher Scientific.

Parlodion solution. Prepare a parlodion solution by weighing 1.5 g of parlodion into a 100-mL volumetric flask and diluting to the mark with isopentyl acetate. The parlodion may take up to 24 hours to completely dissolve. Transfer the parlodion solution to a glass dropping bottle.

Carbon black suspension. Prepare a 0.1 mg/mL suspension of carbon black by adding 50 mg of carbon black to a 500 mL volumetric flask and diluting to the mark with IPA. Transfer the carbon black suspension to a glass dropping bottle.

3.3 Standard preparation

Use only dry, desiccated quartz or cristobalite SRM at room temperature.

Prepare three stock standards by weighing 2, 10, and 100 mg (±0.001 mg) aliquots of quartz or cristobalite. Use the purity of the standard material. For example, SRM 1878a contains 93.7% quartz so 2.134 mg of the material should be used to achieve 2 mg of quartz. Quantitatively transfer the aliquots to separate 200-mL volumetric flasks. Fill the volumetric flasks to about half-volume with 2-propanol. Separately weigh 0.3 mg of carbon black to combine with each of the three aliquots.

Place the stock standards in an ultrasonic bath for 15 minutes to suspend the quartz or cristobalite. Make sure that the water level in the bath is above the level of liquid in the volumetric flasks. Remove the flasks from the bath and allow the suspensions to cool to room temperature. Fill the flasks to the mark with 2-propanol. Invert and shake each flask at least 20 times before immediately transferring the suspensions to 250-mL Erlenmeyer flasks that have ground-glass stoppers. The final concentrations of these stock standards are 10, 50, and 500 µg/mL.

Assemble the filtering apparatus and the liquid nitrogen cold trap. Connect the cold trap to the filtering apparatus to collect the suspending solvent. Solvent vapors should not enter the vacuum line. The diameter at the base of each funnel should be measured and matched to a corresponding measured diameter of a fritted base. This is critical to minimize leaking and attain proper deposition. The diameters of the fritted bases should also match one another. For this validation the fritted area of the bases used measured 16.24 ± 0.08 mm in diameter. The funnels measured 15.98 ± 0.10 mm inner diameter and the funnels were paired with the fritted bases such that each base was no more than 0.30 mm greater in diameter than the funnel with which it was paired.

Center a silver membrane on a fritted base of the filtering apparatus. Place each corresponding funnel atop its matching fritted base and membrane. Secure the funnel to its matching base with a clamp.

Prepare a series of working standards on silver membranes using the 500, 50, and 10 µg/mL stock suspensions by transferring the aliquots shown in Table 3.3 using the procedure described below. Prepare six silver membrane working standards at each microgram level to generate the calibration curves.

Table 3.3
Preparation of Working Standards for Quartz and Cristobalite

stock standards (µg/mL)	aliquot (mL)	working standards (µg)
500	1, 2, 4	500, 1000, 2000
50	1, 2, 5	50, 100, 250
10	1, 2	10, 20

With the vacuum off, add about 5 mL of 2-propanol to each funnel to cushion the stock standard aliquot as it is delivered from the diluter.

Vigorously and repetitively invert and shake the Erlenmeyer flasks to suspend the silica in the IPA. Immediately withdraw each aliquot from the center of the flask at half height of the suspension using the diluter.

Transfer an aliquot to each funnel by placing it in the approximate center of the 2-propanol cushion. A small amount of 2-propanol should be used as a “chaser” to rinse the inside tubing of the diluter after the aliquot is dispensed. The transfer tubing must be sufficiently long to ensure that the suspension never enters the syringes of the auto-diluter. The funnel walls are

rinsed down at this point with 2-propanol until the funnel is filled. The funnel walls should not be rinsed after this point. After the transfer, allow the analyte to settle in the funnel for at least 5 minutes before applying vacuum.

Gently apply vacuum to the filtering apparatus and slowly draw the 2-propanol through it. **Do not rinse the funnel after vacuum has been applied because this may result in an uneven distribution of particulate.** Vacuum should be applied for sufficient time to air dry the membrane. The carbon black will visually show a circular deposition pattern that can later be used to center the deposition in the x-ray beam of the instrument.

For each assembly, carefully remove each funnel by pulling it straight up so that the deposition is not disturbed. Turn the vacuum off. Remove the silver membrane from the fritted-glass base using tweezers after gently sliding a single-edge razor blade between the silver membrane and the base. Place 2 drops of parlodion solution on a glass mirror. Fix the analyte to the membrane by placing the bottom side of the membrane in the parlodion solution so that the parlodion solution is drawn through the membrane by capillary action.

Place a PTFE plastic sheet on top of a hotplate and set the hotplate to 35 °C. Place the silver membrane on top of the heated PTFE sheet to dry the parlodion solution. When the silver membrane is thoroughly dry place the fixed standard in a labeled Petri dish. If the fixed standard is placed in the plastic Petri dish before it is dry, the membrane may become affixed to the dish.

Clean the funnels between standards by rinsing them with IPA and wiping the bottom of each funnel across a clean laboratory towel.

Working standards should be prepared at least annually.

3.4 Sample preparation

3.4.1 Air samples

To achieve a uniform thin layer of material on silver membranes, samples are prepared according to the weight of the sample collected on the PVC filter. This weight is determined using OSHA Method PV2121[34] and falls into one of three ranges: ≥12 mg, between 2 and 12 mg, and ≤2 mg. Preparation technique differs slightly for each range.

Examine all filters to determine if the sampling was performed with the cassette connected backward. If the cassette was connected backward, qualify the sample as having been sampled incorrectly.

Open all samples by removing the filter from its associated cowl and support ring. Note if there are any visible loose non-respirable particles present. In the following steps it is important to ensure all material is quantitatively transferred.

When sample weights are ≥12 mg, prepare samples by carefully removing three representative sample aliquots (scrapes) using a micro spatula to lightly scrape three different places on the sample filter. Each aliquot should weigh approximately 2 mg. Accurately weigh (±0.001 mg) each aliquot onto a separate tared PVC filter. Quantitatively and separately transfer the filters with sample aliquots to individual centrifuge tubes. Add 10 mL of THF to each centrifuge tube to dissolve the PVC filter and to suspend the sample.

[34] Gravimetric Determination (OSHA Method PV2121), 2003. United States Department of Labor, Occupational Safety & Health Administration Web site. https://www.osha.gov/dts/sltc/methods/partial/pv2121/pv2121.html (accessed September 2015).

When sample weights are between 2 and 12 mg, or are ≤2 mg, carefully fold the filter into quarters with the sample inside and use the filter to wipe the cowl inlet. No further wiping is necessary (see Section 4.4). Carefully place the folded filter into an individual centrifuge tube.

When sample weights are between 2 and 12 mg, add enough THF to split the sample into multiple centrifuge tubes. Evenly transfer these aliquots of the sample suspension to multiple centrifuge tubes to result in membrane depositions within the concentration range of the analytical standards. For example, 30 mL of THF are added to a 6-mg sample to give a concentration of about 0.2 mg/mL; this suspension is then split into 3 aliquots in 3 separate centrifuge tubes.

When sample weights are ≤2 mg, add 10 mL of THF to the centrifuge tube to dissolve the PVC filter and to suspend the sample.

Add three drops of a carbon black suspension to each centrifuge tube. Use the vortex mixer to mix the sample. Place the centrifuge tubes in a rack and put the rack into the ultrasonic bath. Make sure that the water level in the bath is above the level of liquid in the centrifuge tubes. Sonicate the sample suspensions for at least 10 minutes. rotating the centrifuge tube rack 90° in the ultrasonic bath at least once to assure even dispersion. Continue sonication until the samples can be transferred as explained below.

Assemble the filtering apparatus and the liquid nitrogen cold trap, as described in Section 3.3.

With the vacuum off, add about 5 mL of THF to each funnel to cushion the addition of the contents from the centrifuge tubes.

Vigorously mix the contents of the centrifuge tube using a vortex mixer and immediately transfer the sample suspensions to the funnels of the vacuum filtering apparatus. With the centrifuge tubes held at about a 45° angle, use a squirt bottle containing THF to rinse any remaining sample into the funnels of the vacuum filtering apparatus. The total volume of THF in the funnels should not exceed 20 mL. After the transfer, allow the analyte to settle in the funnels for at least 5 minutes before applying vacuum. Gently apply vacuum to the filtering apparatus and slowly draw the THF through it. **Do not rinse the funnels after vacuum has been applied because this may result in an uneven distribution of particulate.** Vacuum should be applied for sufficient time to air dry the silver membranes. The carbon black will visually show a circular deposition pattern that can later be used to center the deposition in the x-ray beam of the instrument.

For each assembly, carefully remove each funnel by pulling it straight up so that the deposition is not disturbed. Turn the vacuum off. Remove the silver membrane from the fritted-glass base using tweezers after gently sliding a single-edge razor blade between the silver membrane and the base. Place 2 drops of parlodion solution on a glass mirror. Fix the sample to the membrane by placing the bottom side of the membrane in the parlodion solution so that the parlodion solution is drawn through the membrane by capillary action.

Place a PTFE plastic sheet on top of a hotplate and set the hotplate to 35 °C. Place the silver membrane on top of the heated PTFE sheet to dry the parlodion solution. When the silver membrane is thoroughly dry place the fixed sample in a labeled Petri dish. If the fixed sample is placed in the plastic Petri dish before it is dry, the membrane may become affixed to the dish.

Samples that have been noted to contain visible loose particles, or have an unusually high weight may be inspected under a microscope to determine if large particles or clumps are present. Very large particles indicate the material is non-respirable and must be reported as such. Clumping on the silver membrane indicates inadequate dispersion. The sample must be redeposited as described in Appendix A, Interference Acid Digestion Procedure, if a significant amount of clumping is present.

Clean the funnels between samples by rinsing them with THF and wiping the bottom of each funnel across a clean laboratory towel.

3.4.2 Bulk samples

All bulk samples should be sized with a 325-mesh sieve (44 µm). If the particle size of the bulk sample is larger than about 44-µm, grind a representative portion of the sample to a fine powder using either a mortar and pestle or a freezer mill prior to sizing the sample. Material passing through the sieve will have a particle size less than 44-µm. Weigh between 0.15 and 0.20 mg of the sieved sample onto a PVC filter and place it into a centrifuge tube.

Add 10 mL of THF to the weighed sample in the centrifuge tube to dissolve the PVC filter and to suspend the sample. Add three drops of a carbon black suspension the centrifuge tube. Use the vortex mixer to mix the sample. Place the centrifuge tubes in a rack and put the rack into the ultrasonic bath. Make sure that the water level in the bath is above the level of liquid in the centrifuge tubes. Sonicate the sample suspension for at least 10 minutes. rotating the centrifuge tube rack 90° in the ultrasonic bath at least once to assure even dispersion. Continue sonication until the samples can be transferred. Deposit the sample on a silver membrane as described in section 3.4.1.

Clean the funnels between samples by rinsing them with THF and wiping the bottom of each funnel across a clean laboratory towel.

3.5 Analysis

3.5.1 Instrument calibration

Refer to the XRD instrument manufacturer's manual for system startup and initialization procedures. Optimize the instrument, including scanning increments and counting times to detect sufficiently low amounts of analyte. Determine the location of the silver diffraction angle (actual 44.33° 2θ) with each standard analysis. The location of the secondary silver diffraction angle is used as an initial reference point and adjustments to diffraction angle locations are made by the instrument software as necessary.

For this method validation, silver membranes were rotated at a rate of 120 rpm while being analyzed with a step width of 0.020° and a count value of 5000 counts for each analytical diffraction angle (step width 0.010° and 64000 counts for the silver diffraction angle) with 50 kV and 300 mA instrument power settings. Calibrate the instrument prior to analyzing samples. Prepare separate calibrations for each diffraction angle of quartz and cristobalite. The instrument is calibrated at least semi-annually or sooner if needed. Recalibration is also performed after service or maintenance that affects the calibration. Normal analytical angle parameters and instrument settings are given in Table 3.5.1.1.

Table 3.5.1.1
Normal Analytical Angle Parameters

quartz	scanning range	2θ values (°) location	peak range	*d*
primary	25.90 to 27.20	26.66	26.61 to 26.71	3.34
secondary	20.06 to 21.40	20.88	20.83 to 20.93	4.25
tertiary	49.40 to 50.70	50.18	50.13 to 50.23	1.82
quaternary	59.40 to 60.70	60.00	59.95 to 60.10	1.54
cristobalite	**scanning range**	**2θ values (°) location**	**peak range**	***d***
primary	21.20 to 22.50	22.00	21.95 to 22.05	4.05
secondary	35.50 to 36.80	36.07	36.02 to 36.12	2.49
tertiary	30.76 to 32.06	31.42	31.37 to 31.47	2.85

Note: Angle locations are dependent on instrument and sample conditions and may vary slightly. d is the constant spacing between discrete parallel lattice planes in a crystalline solid.

Use the visible carbon black to center the standards on the auto sampler mounts so they are centered in the X-ray beam. Analyze the calibration standards using the optimized conditions determined and then evaluate the resultant data. The analytical data should be statistically weighted or transformed to reduce the effect of measurement errors. SLTC has developed a Microsoft Excel spreadsheet with specialized macro commands to transform both detector response (y-axis) and mass (x-axis) data. Three data transforms are calculated at SLTC when preparing a new calibration. They are square root, logarithm, and fourth root.

Logarithmic transforms are the most common transforms used at SLTC and were used in the validation of this method. A logarithmic transform converts the approximate geometric series of mass data along the abscissa into more equally-spaced data which helps make a third order polynomial fit well conditioned and helps prevent non-monotonic curve 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 µg) prior to the logarithmic transform. The offset is removed when the inverse transform is taken to process data.

Figures 3.5.1.1 through 3.5.1.4 show examples of calibration transforms for each of the four angles used in analysis for quartz. Figures 3.5.1.5 through 3.5.1.8 are scans from the XRD instrument at the target concentration for quartz. Figures 3.5.1.9 through 3.5.1.11 show examples of calibration transforms used for each of the three angles used in analysis of cristobalite. Figures 3.5.1.12 through 3.5.1.14 are scans from the XRD instrument at the target concentration for cristobalite. The data for these calibrations are given in Tables 3.5.1.2 and 3.5.1.3.

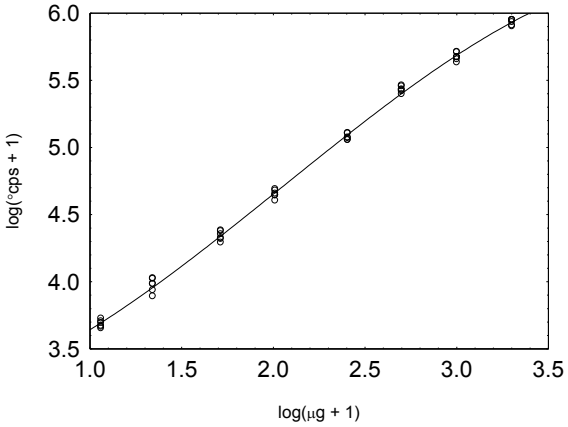

Figure 3.5.1.1. Primary angle calibration for quartz with logarithmic transform $y = -0.0772x^3 + 0.475x^2 + 0.125x + 3.12$.

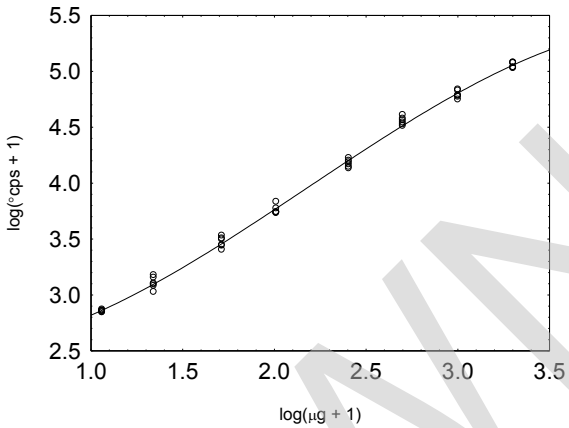

Figure 3.5.1.2. Secondary angle calibration for quartz with logarithmic transform $y = -0.0912x^3 + 0.596x^2 – 0.208x + 2.52$.

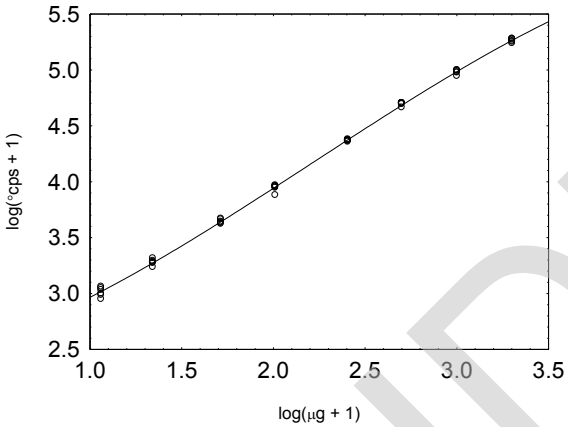

Figure 3.5.1.3. Tertiary angle calibration for quartz with logarithmic transform $y = -0.0531x^3 + 0.352x^2 + 0.289x + 2.38$.

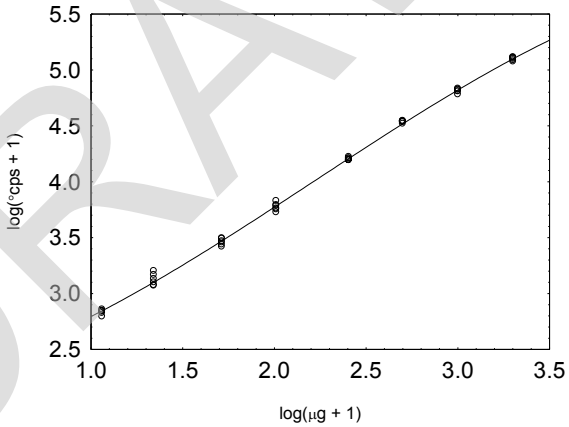

Figure 3.5.1.4. Quaternary angle calibration for quartz with logarithmic transform $y = -0.0554x^3 + 0.368x^2 + 0.263x + 2.22$.

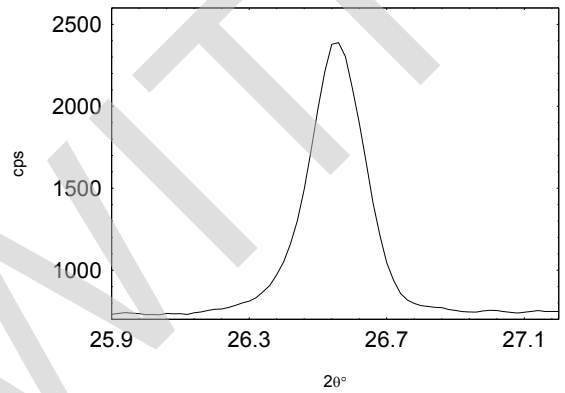

Figure 3.5.1.5. Primary angle scan of quartz at the target concentration.

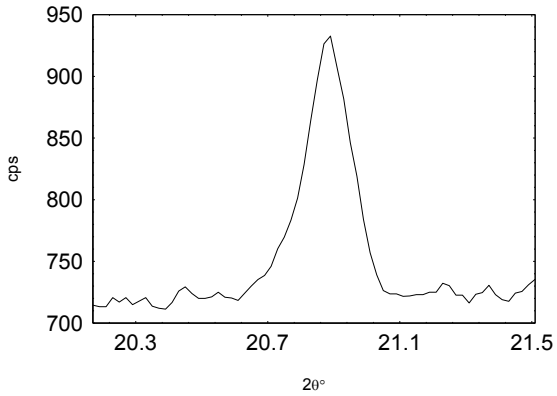

Figure 3.5.1.6. Secondary angle scan of quartz at the target concentration.

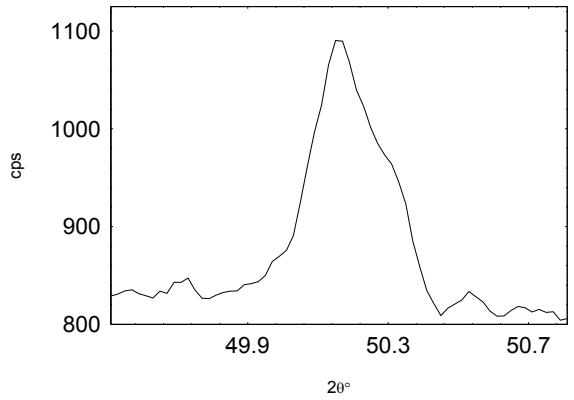

Figure 3.5.1.7. Tertiary angle scan of quartz at the target concentration.

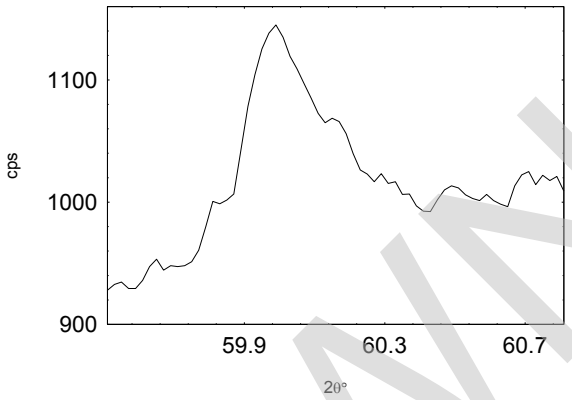

Figure 3.5.1.8. Quaternary angle scan of quartz at the target concentration.

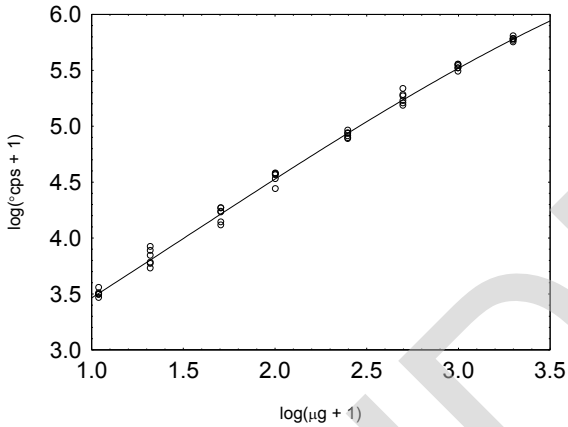

Figure 3.5.1.9. Primary angle calibration for cristobalite with logarithmic transform $y = -0.0240x^3 + 0.108x^2 + 0.907x + 2.47$.

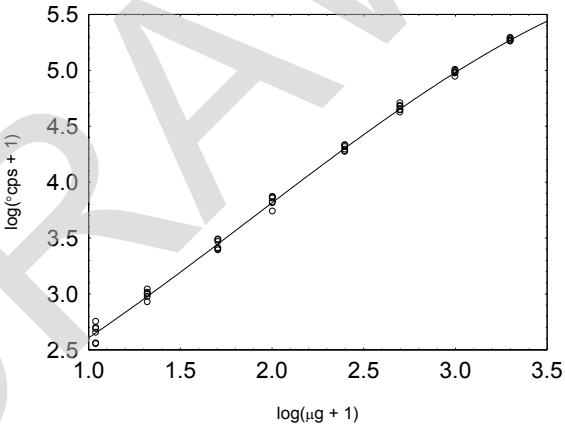

Figure 3.5.1.10. Secondary angle calibration for cristobalite with logarithmic transform $y = -0.0586x^3 + 0.332x^2 + 0.621x + 1.71$.

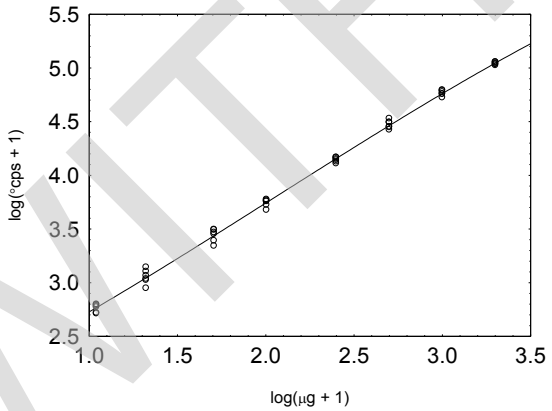

Figure 3.5.1.11. Tertiary angle calibration for cristobalite with logarithmic transform $y = -0.0251x^3 + 0.154x^2 + 0.727x + 1.87$.

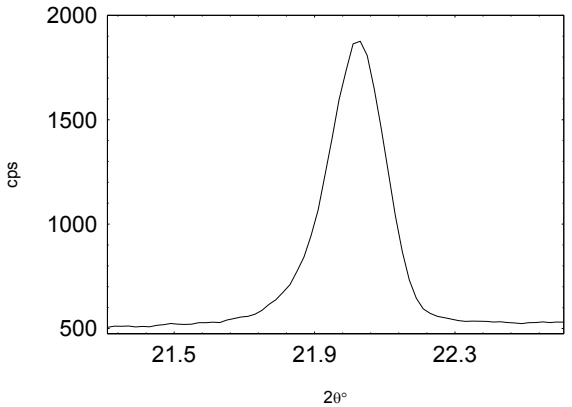

Figure 3.5.1.12. Primary angle scan of cristobalite at the target concentration.

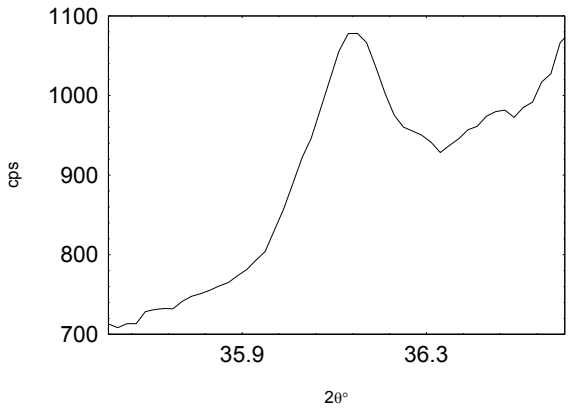

Figure 3.5.1.13. Secondary angle scan of cristobalite at the target concentration.

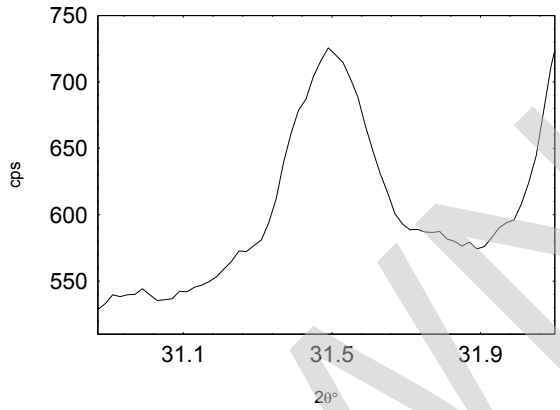

Figure 3.5.1.14. Tertiary angle scan of cristobalite at the target concentration.

Table 3.5.1.2
Calibration Data for Quartz

standard mass (µg)	primary (°cps)	secondary (°cps)	tertiary (°cps)	quaternary (°cps)
10.5	4937	728	973	722
10.5	4694	716	1078	699
10.5	5326	722	1155	623
10.5	4504	700	1121	671
10.5	5080	742	998	688
10.5	4624	701	894	703
21	10511	1505	1724	1353
21	9627	1430	2068	1466
21	10634	1245	1919	1595
21	8640	1265	1890	1259
21	9650	1205	1964	1191
21	7782	1064	1879	1177
50.7	22618	3202	4326	2624
50.7	19568	2535	4201	3095
50.7	23829	3134	4276	2746
50.7	21136	2755	4398	2935
50.7	24146	3398	4686	3125
50.7	20842	2786	4608	2869
101.4	45388	5528	9303	5659
101.4	43928	5468	9069	6192
101.4	48983	5951	9172	6735
101.4	44040	5453	8822	5763
101.4	47808	6820	8946	6074
101.4	40182	5394	7602	5333
253.5	118817	14015	23280	15604
253.5	113521	13562	23577	15575
253.5	128255	15875	24010	16223
253.5	127046	16788	23609	16673
253.5	117426	15367	23186	15756
253.5	113893	14736	22784	16104
500.3	289869	37805	50472	35110
500.3	262023	32462	50689	34616
500.3	270635	33608	50780	34134
500.3	267400	36465	50024	34775
500.3	285513	40813	49456	34540
500.3	249658	34850	46171	33016
1000.6	515136	67378	97973	68140
1000.6	454223	59281	95632	64314
1000.6	511622	68882	99902	66777
1000.6	469322	60580	99327	66572
1000.6	470152	61077	94686	64590
1000.6	430105	56023	88346	60364
2001.2	892142	118453	181464	125543
2001.2	810811	107363	178692	122324
2001.2	859260	109038	186716	128396
2001.2	888390	120308	190279	128764
2001.2	889316	119670	190638	130029
2001.2	798056	106853	173360	118843

Table 3.5.1.3
Calibration Data for Cristobalite

standard mass (µg)	primary (°cps)	secondary (°cps)	tertiary (°cps)
10.0	3200	563	629
10.0	3107	356	516
10.0	3115	362	608
10.0	3125	498	621
10.0	3585	450	592
10.0	2909	485	524
20.0	8329	1000	1271
20.0	6013	842	888
20.0	7673	1095	1392
20.0	5873	987	1057
20.0	6935	941	1162
20.0	5335	1027	1085
50.0	18507	2914	2937
50.0	16941	2517	2834
50.0	18400	3065	3124
50.0	13806	2565	2457
50.0	17156	3030	3100
50.0	12968	2454	2201
100.0	36391	7142	5858
100.0	37424	7269	5725
100.0	37842	7376	5967
100.0	33658	6586	5299
100.0	36938	6487	5735
100.0	27426	5468	4745
250.0	86563	20622	14195
250.0	81176	19531	13862
250.0	85328	21237	14700
250.0	78204	18919	13403
250.0	91389	21370	14651
250.0	76680	18617	12877
500.0	215318	50791	33757
500.0	160152	44256	28364
500.0	190084	47275	31177
500.0	168161	43839	27989
500.0	152405	41891	26529
500.0	184921	48000	31054
1000.0	345208	96308	59833
1000.0	307577	87562	52976
1000.0	353155	98745	62285
1000.0	328663	94567	57068
1000.0	355655	100973	61566
1000.0	328842	93823	57343
2000.0	636866	193103	113637
2000.0	597444	184195	108526
2000.0	581235	194778	113673
2000.0	603151	181755	108856
2000.0	600733	188052	110958
2000.0	562374	181325	105687

Select calibration standards to be used as calibration verification standards that are analyzed during routine sample analysis. Standards used to calculate calibration curves are stable throughout the useful lifetime of the calibration.

XRD instrumentation is generally stable making calibration curves useful for a period of time. A new calibration is required when results from calibration verification standards fail internal quality system requirements or when instrument operation parameters change.

3.5.2 Sample analysis

Use the visible carbon black to center the samples and calibration verification standards on the auto sampler mounts so they are centered in the X-ray beam. Scan the samples and calibration verification standards using the optimized conditions determined in Section 3.5.1.1.

Determine the location of the silver diffraction angle (actual 44.33° 2θ) with each sample analysis. The location of the secondary silver diffraction angle is used as an initial reference point for each sample. If the silver angle intensity of a sample is noticeably less than for a calibration verification standard, then significant self-absorption of X-rays has occurred. This is most likely caused by the sample matrix and can be remedied by the acid digestion procedure described in Appendix A.

The presence and amount of quartz or cristobalite is determined by the physical location of the local maximum intensities for each analytical diffraction angle and by the intensity at each angle. This intensity gives rise to an analytical signal peak. Compare the calculated exposure from the primary peak with the exposure limit. For samples with air volumes >500 L, if the calculated exposure is less than 0.75 times the exposure limit the analysis is ended without scanning other diffraction peaks. The result is reported as “less than or equal to” the result of the primary peak. Samples with air volumes <500 L are also ended in this manner, if the exposure is less than 0.5 times the exposure limit.

Maximum peak intensities must be present on all four angles in order to report quartz (all three for cristobalite). This means that the local maximum intensity must be within the peak range listed in Table 3.5.1.1 for each angle and the result of each angle must be greater than or equal to its DLOP (see Section 4.1) in order to report any analyte.

Visually inspect data for interference which may appear as occurrence of multiple peaks, shoulders, or unusual broadening at the base of the peaks. Interference is often accompanied by disagreement in the amount of quartz or cristobalite among multiple analytical diffraction peaks. Evaluate different approaches for peak area integration to alleviate the effects of interference.

Interference effects are minimized by evaluating each sample for confirmation using multiple peaks but excluding those peaks which show signs of interference. Peaks confirm one another when the mathematical agreement of their results is similar to the agreement of calibration standard peaks which are free from interference.[35]

When there are at least two confirming peaks crystalline silica can be reported. Values that are greater than the DLOP but less than the RQL of the analytical angle may be used for confirmation but not for reporting. Final results are calculated only from peaks

[35] Reznik, I.; Johansen, D. Concentration-Dependent Confirmation Model of Quartz X-Ray Diffraction Analysis, 2015. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/studies/quartz_xray_diffraction.pdf (accessed September 2015).

that are greater than or equal to the RQL of the analytical angle (see Section 4.1) and appear free from interference. The majority of interferences are positive, meaning the peaks that do not confirm are usually (but not always) those that give the highest results. Often the confirming peaks are the low pair (or the low three).

The absence of a confirming pair of peaks is a result of severe interference. These samples are subjected to the acid digestion technique described in Appendix A to remove the interferences.

3.6 Interferences (analytical)

This analytical method for crystalline silica is not a chemical or elemental analysis. It is based on the positions of atoms that make up the crystal lattice and the distances between planes of atoms. Anything that changes the structure will change the diffraction patterns produced by the crystal. Each crystalline silica polymorph (α-quartz, cristobalite, trydimite, etc.) has slightly different crystal structures and thus different patterns. Particle size of the material on the silver membrane can affect X-ray instrument response. It is possible for a mineral other than crystalline silica to produce a pattern that will have some of the elements of a crystalline silica pattern. For example, feldspars interfere with the primary peak of quartz but do not interfere with the secondary and tertiary peaks. Examples of analytical interferences are shown in Appendix B. These interferences may be resolved by using alternate diffraction peaks that confirm one another or by performing the acid digestion procedure as described in Appendix A. Substances are listed in Appendix B as a potential interferent if one or more strong diffraction peaks of the substance come within ± 0.65° of 2θ, the theoretical analyte diffraction angle. Some of the listed interferences may only become a problem when a large amount of the interfering substance is present. The majority of the interferences listed in Appendix B will most likely not be present together when sampling industrial operations which produce quartz or cristobalite exposures. Exotic substances found only in research settings are not included and the list is not definitive. Quartz is the only substance to have all four analytical diffraction peaks within ± 0.20° of 2θ of the theoretical angles.

Inverting the sample assembly and spilling the contents of the cyclone grit pot onto the sample filter causes unreliable results. The particle-size distribution of non-respirable samples that do not approximate the size distribution of the respirable standard material can also cause unreliable results.

3.7 Calculations

The amount of silica determined in Section 3.5.2 is used in the following equations to calculate the percent crystalline silica in the dust and this value is used to determine the PEL. Samples collected without a cyclone or at a sampling rate other than that which is recommended (1.7 ± 0.2 L/min) are considered non-respirable samples. Although these samples are calculated in the same manner as respirable samples the result are reported using IMIS codes S103 or S105.

Percent by weight of quartz (or cristobalite) in the sample is calculated by:

$$\%\, SiO_2 = \frac{M_t}{sample\ weight}\ 100\%$$

where *% SiO_2* is concentration by percent (% quartz or cristobalite)
M_t is total micrograms silica per sample
sample weight is microgram weight determined by gravimetric analysis of the filter

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The quartz PEL in mg/m^3 is calculated separately for each sample using the mass formula:

$$\frac{10\ mg/m^3}{\%\, SiO_2\ +\ 2}$$

The cristobalite PEL in mg/m^3 is calculated separately for each sample. Use ½ the value calculated from the mass formula for quartz.

where *% SiO_2* is concentration by percent (% quartz or cristobalite)

If the sample extract needed to be split into aliquots because the mass collected on the PVC filter was greater than 2 mg; then add the individual analytical results to calculate the total µg per sample:

$$M_t = M_1 + M_2 + M_3 + \cdots + M_n$$

where *M_t* is total micrograms silica per sample
M_1, M_2, M_3,…,M_n are the microgram results from each aliquot

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If the sample mass collected was greater than or equal to 12 mg and 3 scrapes were taken from the sample; then % SiO_2 is calculated individually for each scrape and the mean of the three results is calculated and used in the mass formula for the PEL:

$$\%\, SiO_2 = \left[\frac{M_1}{scrape_1} + \frac{M_2}{scrape_2} + \frac{M_3}{scrape_3}\right]\frac{1}{3}\ (100\%)$$

where *% SiO_2* is concentration by percent (% quartz or cristobalite)
M_1, M_2, and *M_3* are the microgram results from each scrape
$scrape_1$, $scrape_2$, and *$scrape_3$* are the masses of each scrape in micrograms

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Silica concentration by weight for bulk samples is calculated by:

$$\%\, SiO_2 = \frac{M_t}{bulk\ weight}\ 100\%$$

where *% SiO_2* is concentration by percent in the bulk (% quartz or cristobalite)
M_t is total micrograms silica per sample
bulk weight is the bulk sample weight in micrograms

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4. Method Validation

Where applicable, this method follows validation protocols drawing from the OSHA SLTC "Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis".[36] These Guidelines detail required validation tests, show examples of statistical calculations, list validation acceptance criteria, and define analytical parameters. The unique nature of silica and its analysis prevented strict adherence to these guidelines.

4.1 Detection limit of the overall procedure (DLOP) and reliable quantitation limit (RQL)

Quartz

The DLOP is measured as mass per sample and is expressed as air concentration based on the recommended sampling parameters. Twelve low ash PVC filters were spiked with equally descending increments of analyte, such that the highest membrane loading was 24 µg. This is the amount spiked on a filter that would produce a peak approximately 12 times the response of a blank sample. These spiked filters and a filter blank were analyzed, and the data obtained used to calculate the required parameters (standard estimate of error and the slope or analytical sensitivity) for the calculation of the DLOP. The test was conducted with six sets of replicates simultaneously and the parameters were calculated six times in order to account for differences in aliquot suspension spikes. Each replicate set was prepared on one of each of six fritted bases and corresponding funnels used by SLTC for the preparation of silica samples. The values for each parameter are reported for each diffraction angle in Tables 4.1.1 through 4.1.4. The mean values of 361 and 342 for the slope (m) and standard error of estimate (SEE) respectively were obtained for the primary diffraction angle. The mean DLOP for the primary diffraction angle was calculated to be 2.84 µg/sample (3.48 µg/m^3).

Table 4.1.1
Parameters for Quartz on the Primary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
SEE	291	234	339	375	437	377	342	71.6
m	356	341	374	339	384	371	361	18.5
DLOP	2.46	2.07	2.72	3.31	3.42	3.05	2.84	0.520

Table 4.1.2
Parameters for Quartz on the Secondary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
SEE	58.0	96.2	103	84.8	70.0	95.2	84.5	17.4
m	52.2	45.1	47.6	46.0	51.8	46.7	48.2	3.03
DLOP	3.33	6.40	6.49	5.53	4.05	6.11	5.32	1.32

Table 4.1.3
Parameters for Quartz on the Tertiary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
SEE	118	103	80.1	106	150	108	111	22.9
m	72.3	73.8	77.6	68.9	73.6	72.6	73.1	2.81
DLOP	4.88	4.20	3.10	4.62	6.10	4.47	4.56	0.974

Table 4.1.4
Parameters for Quartz on the Quaternary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
SEE	127	86.2	118	97.7	121	67.5	103	23.2
m	57.4	52.4	54.0	47.9	51.9	53.3	52.8	3.09
DLOP	6.66	4.93	6.58	6.12	6.98	3.81	5.85	1.23

[36] Eide, M.; Simmons, M.; Hendricks, W. Validation Guidelines for Air Sampling Methods Utilizing Chromatographic Analysis, 2010. United States Department of Labor, Occupational Safety & Health Administration Web site. http://www.osha.gov/dts/sltc/methods/chromguide/chromguide.pdf (accessed September 2015).

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of the DLOP providing 75% to 125% of the analyte is recovered. The RQL and recoveries near the RQL were calculated six times. The RQL and recovery data are reported for each angle in Tables 4.1.5 through 4.1.8. The mean RQL for quartz for the primary diffraction angle is 9.76 µg/sample (12.0 µg/m^3). The mean recovery for quartz at this concentration on the primary diffraction angle is 104%. Tables 4.1.9 through 4.1.12 and their accompanying figures show a sample regression line for each diffraction angle. The sample regression line displayed shows the data set that most closely matches the mean. All data are included as Table 4.1.13. Figures 4.1.5 through 4.1.8 are scans from the XRD instrument of the RQL for each angle for quartz.

Table 4.1.5
RQL and Recovery Data for Quartz on the Primary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
RQL	8.19	6.88	9.06	11.0	11.4	12.0	9.76	2.02
recovery (%)	90.7	115	111	100	110	97.9	104	9.34

Table 4.1.6
RQL and Recovery Data for Quartz on the Secondary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
RQL	11.1	21.3	21.6	18.5	13.5	20.4	17.7	4.41
recovery (%)	85.0	119	104	104	99.4	92.0	101	11.7

Table 4.1.7
RQL and Recovery Data for Quartz on the Tertiary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
RQL	16.3	14.0	10.3	15.4	20.3	14.9	15.2	3.25
recovery (%)	112	88.5	78.7	99.7	93.1	108	96.7	12.4

Table 4.1.8
RQL and Recovery Data for Quartz on the Quaternary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
RQL	22.2	16.4	22.0	20.4	23.3	12.7	19.5	4.11
recovery (%)	110	100	108	89.9	101	97.9	101	7.26

Table 4.1.9
Detection Limit of the Overall Procedure
Quartz Primary Diffraction Angle

mass per sample (µg)	°cps
0	800
2	816
4	1697
6	1899
8	2780
10	4384
12	4812
14	5685
16	6348
18	6654
20	7725
22	8670
24	9164

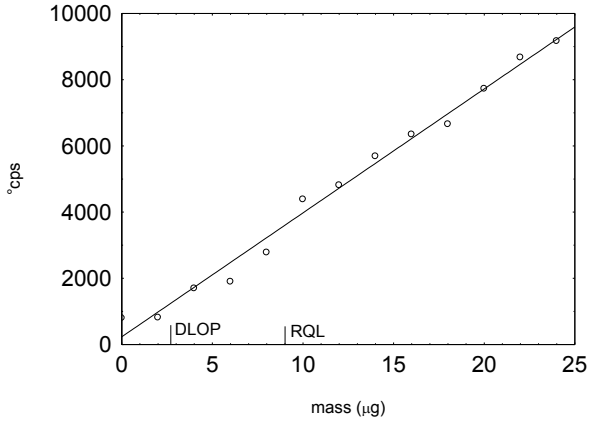

Figure 4.1.1. Example plot of data to determine the DLOP/RQL for quartz on the primary diffraction angle y = 374x + 233 (sample set 3).

Table 4.1.10
Detection Limit of the Overall Procedure
Quartz Secondary Diffraction Angle

mass per sample (µg)	°cps
0	43
2	129
4	186
6	183
8	285
10	566
12	631
14	640
16	680
18	875
20	1000
22	1128
24	966

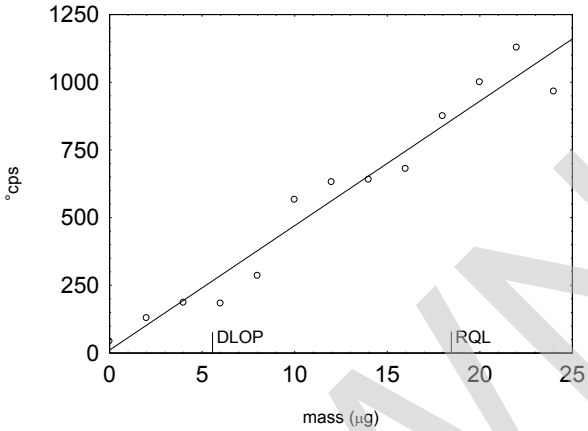

Figure 4.1.2. Example plot of data to determine the DLOP/RQL for quartz on the secondary diffraction angle y = 46.0x + 11.0 (sample set 4).

Table 4.1.11
Detection Limit of the Overall Procedure
Quartz Tertiary Diffraction Angle

mass per sample (µg)	°cps
0	26
2	180
4	160
6	439
8	592
10	479
12	764
14	946
16	1081
18	1423
20	1266
22	1595
24	1559

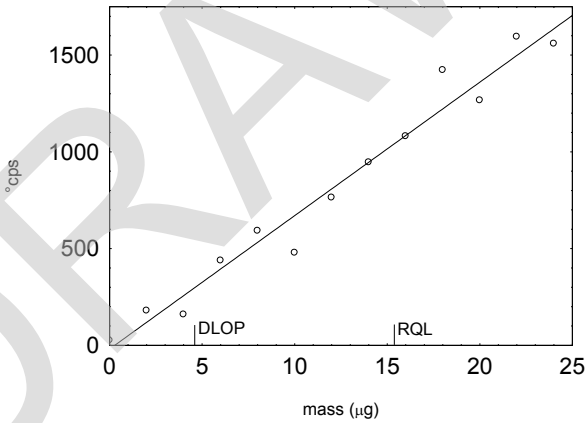

Figure 4.1.3. Example plot of data to determine the DLOP/RQL for quartz on the tertiary diffraction angle y = 68.9x - 18.8 (sample set 4).

Table 4.1.12
Detection Limit of the Overall Procedure
Quartz Quaternary Diffraction Angle

mass per sample (µg)	°cps
0	20
2	105
4	322
6	210
8	196
10	515
12	472
14	642
16	658
18	840
20	839
22	1116
24	1249

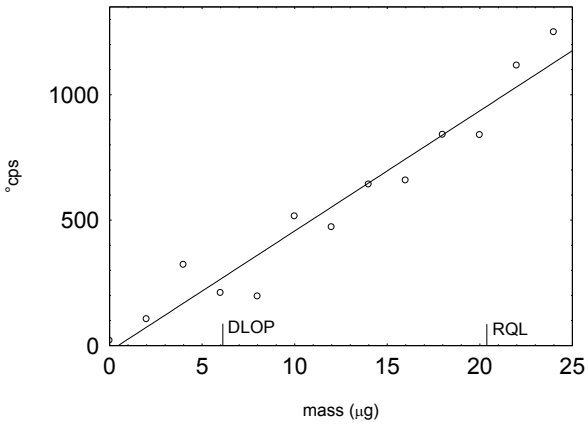

Figure 4.1.4. Example plot of data to determine the DLOP/RQL for quartz on the quaternary diffraction angle y = 47.9x - 22.3 (sample set 4).

Table 4.1.13
Detection Limit of the Overall Procedure for Quartz

sample set	mass /sample (µg)	primary angle (°cps)	secondary angle (°cps)	tertiary angle (°cps)	quaternary angle (°cps)	sample set	mass /sample (µg)	primary angle (°cps)	secondary angle (°cps)	tertiary angle (°cps)	quaternary angle (°cps)
1	0	514	82	169	194	4	0	40	43	26	20
1	2	932	80	59	67	4	2	995	129	180	105
1	4	1600	273	157	174	4	4	1434	186	160	322
1	6	1990	224	416	111	4	6	2172	183	439	210
1	8	2767	368	442	319	4	8	2810	285	592	196
1	10	3933	478	649	496	4	10	3629	566	479	515
1	12	4337	522	942	526	4	12	4218	631	764	472
1	14	5010	718	1072	681	4	14	5602	640	946	642
1	16	6329	837	1282	1054	4	16	4920	680	1081	658
1	18	6380	962	1302	973	4	18	6089	875	1423	840
1	20	7012	1009	1430	1015	4	20	6357	1000	1266	839
1	22	8494	1185	1378	1342	4	22	8017	1128	1595	1116
1	24	8628	1273	1813	1344	4	24	8486	966	1559	1249
2	0	47	27	145	2	5	0	241	48	23	68
2	2	693	103	125	86	5	2	849	105	190	31
2	4	1353	85	256	140	5	4	1466	120	79	219
2	6	2369	138	272	209	5	6	2216	348	421	273
2	8	2862	364	730	262	5	8	2811	364	670	354
2	10	3155	455	680	331	5	10	4080	549	733	417
2	12	4062	594	868	658	5	12	5157	565	920	604
2	14	4799	630	918	571	5	14	5042	717	1136	832
2	16	5192	547	1333	771	5	16	6551	817	1027	542
2	18	6246	718	1343	979	5	18	7513	1044	1687	792
2	20	6610	773	1514	865	5	20	8225	1080	1371	1210
2	22	7320	1155	1568	1169	5	22	7582	998	1519	1159
2	24	8692	1048	1805	1203	5	24	9355	1280	1702	1225
3	0	800	184	28	33	6	0	1	53	23	12
3	2	816	130	151	97	6	2	826	85	249	0
3	4	1697	315	288	27	6	4	1291	93	197	128
3	6	1899	228	325	32	6	6	1968	276	306	150
3	8	2780	439	604	397	6	8	2958	364	541	250
3	10	4384	544	555	363	6	10	4647	539	861	538
3	12	4812	718	795	591	6	12	4346	675	752	538
3	14	5685	652	1040	778	6	14	4650	507	1078	615
3	16	6348	744	1233	638	6	16	5535	747	1008	746
3	18	6654	1156	1356	833	6	18	6978	914	1358	953
3	20	7725	1054	1418	845	6	20	7388	862	1304	902
3	22	8670	1170	1696	1179	6	22	8284	1189	1686	1122
3	24	9164	1128	1888	1311	6	24	8868	1014	1773	1212

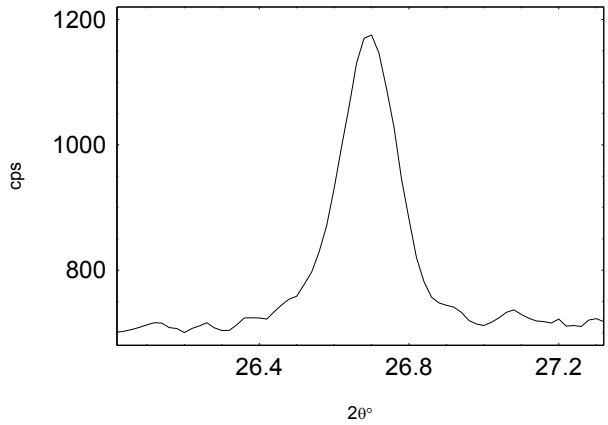

Figure 4.1.5. Scan of quartz at the RQL of the primary angle.

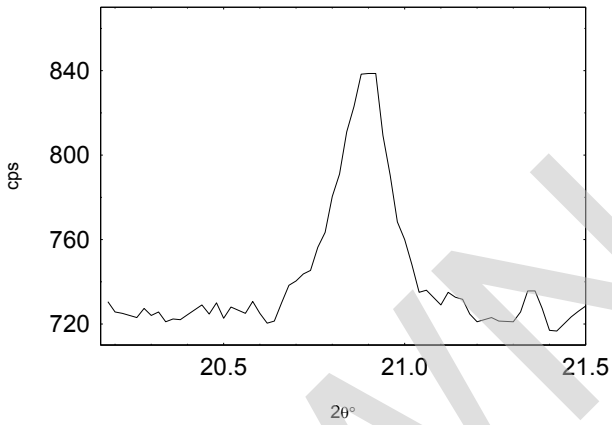

Figure 4.1.6. Scan of quartz at the RQL of the secondary angle.

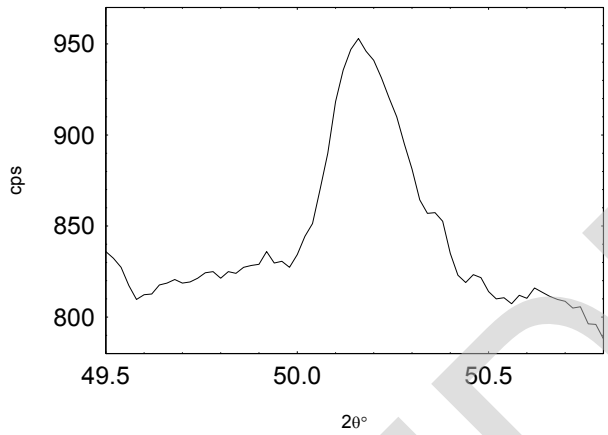

Figure 4.1.7. Scan of quartz at the RQL of the tertiary angle.

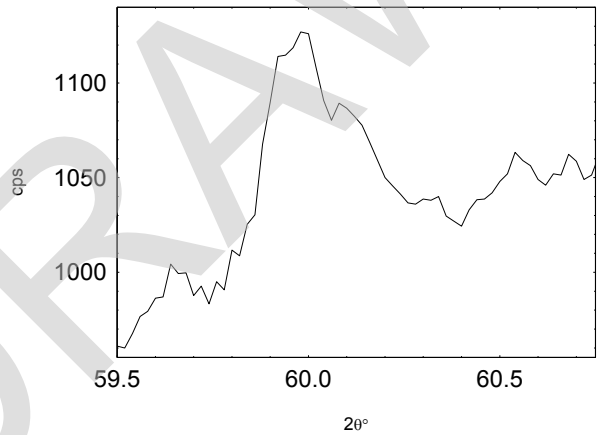

Figure 4.1.8. Scan of quartz at the RQL of the quaternary angle.

Cristobalite

The DLOP is measured as mass per sample and is expressed as air concentration based on the recommended sampling parameters. Twelve low ash PVC filters were spiked with equally descending increments of analyte, such that the highest membrane loading was 36 µg. This is the amount spiked on a filter that would produce a peak approximately 12 times the response of a blank sample. These spiked filters and a filter blank were analyzed, and the data obtained used to calculate the required parameters (standard estimate of error and the slope or analytical sensitivity) for the calculation of the DLOP. The test was conducted with six sets of replicates simultaneously and the parameters were calculated six times in order to account for differences in aliquot suspension spikes. Each replicate set was prepared on one of each of six fritted bases and corresponding funnels used by SLTC for the preparation of silica samples. The values for each parameter are reported for each diffraction angle in Tables 4.1.14 through 4.1.16. The mean values of 301 and 616 for the slope (m) and standard error of estimate (SEE) respectively were obtained for the primary diffraction angle. The mean DLOP for the primary diffraction angle was calculated to be 6.17 µg/sample (7.56 µg/m^3).

Table 4.1.14
Parameters for Cristobalite on the Primary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
SEE	563	669	579	608	631	647	616	40.6
m	311	293	323	282	325	274	301	21.5
DLOP	5.43	6.85	5.38	6.46	5.83	7.09	6.17	0.732

Table 4.1.15
Parameters for Cristobalite on the Secondary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
SEE	93.7	113	156	104	80.8	82.8	105	27.8
m	48.5	47.0	49.8	42.6	53.0	42.6	47.3	4.11
DLOP	5.80	7.20	9.39	7.34	4.58	5.84	6.69	1.67

Table 4.1.16
Parameters for Cristobalite on the Tertiary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
SEE	99.4	101	112	90.5	192	89.8	114	39.0
m	50.6	43.4	50.3	44.4	55.6	42.5	47.8	5.18
DLOP	5.89	6.99	6.67	6.11	10.4	6.34	7.07	1.68

The RQL is considered the lower limit for precise quantitative measurements. It is determined from the regression line parameters that were obtained for the calculation of the DLOP providing 75% to 125% of the analyte is recovered. The RQL and recoveries near the RQL were calculated six times. The RQL and recovery data are reported for each angle in Tables 4.1.17 through 4.1.19. The mean RQL for cristobalite for the primary diffraction angle is 20.6 µg/sample (25.2 µg/m^3). The mean recovery for cristobalite at this concentration on the primary diffraction angle is 107%. Tables 4.1.20 through 4.1.22 and their accompanying figures show a sample regression line for each diffraction angle. The sample regression line displayed shows the data set that most closely matches the mean. All data are included as Table 4.1.23. Figures 4.1.12 through 4.1.14 are scans from the XRD instrument of the RQL for each angle for cristobalite.

Table 4.1.17
RQL and Recovery Data for Cristobalite on the Primary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
RQL	18.1	22.8	18.0	21.5	19.4	23.6	20.6	2.41
recovery (%)	103	111	92.8	121	109	107	107	9.31

Table 4.1.18
RQL and Recovery Data for Cristobalite on the Secondary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
RQL	19.3	24.0	33.0	24.5	15.3	19.5	22.6	6.12
recovery (%)	115	105	95.2	92.5	96.5	110	102	9.03

Table 4.1.19
RQL and Recovery Data for Cristobalite on the Tertiary Diffraction Angle

base	1	2	3	4	5	6	mean	*s*
RQL	19.6	23.3	22.2	20.4	34.5	21.1	23.5	5.54
recovery (%)	109	91.9	113	111	97.3	119	107	10.2

Table 4.1.20
Detection Limit of the Overall Procedure
Cristobalite Primary Diffraction Angle

mass per sample (µg)	°cps
0	78
3	875
6	1588
9	2327
12	3068
15	4525
18	6178
21	7305
24	6738
27	7671
30	9149
33	8609
36	9928

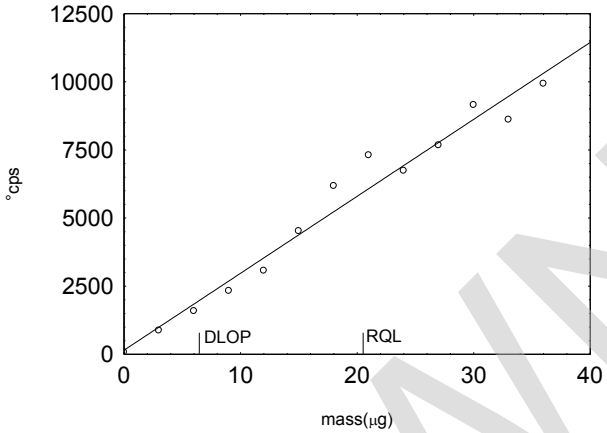

Figure 4.1.9. Example plot of data to determine the DLOP/RQL for cristobalite on the primary diffraction angle y = 282x + 151 (sample set 4).

Table 4.1.21
Detection Limit of the Overall Procedure
Cristobalite Secondary Diffraction Angle

mass per sample (µg)	°cps
0	4
3	28
6	117
9	294
12	390
15	326
18	563
21	931
24	1040
27	1066
30	1216
33	1395
36	1703

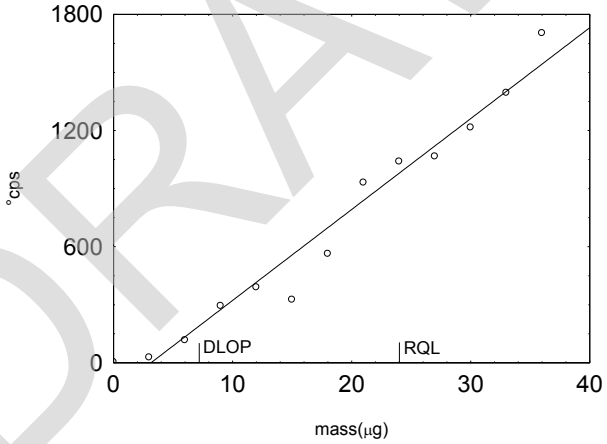

Figure 4.1.10. Example plot of data to determine the DLOP/RQL for cristobalite on the secondary diffraction angle y = 47.0x - 148 (sample set 2).

Table 4.1.22
Detection Limit of the Overall Procedure
Cristobalite Tertiary Diffraction Angle

mass per sample (µg)	°cps
0	118
3	79
6	270
9	314
12	420
15	729
18	754
21	1110
24	967
27	1318
30	1239
33	1377
36	1588

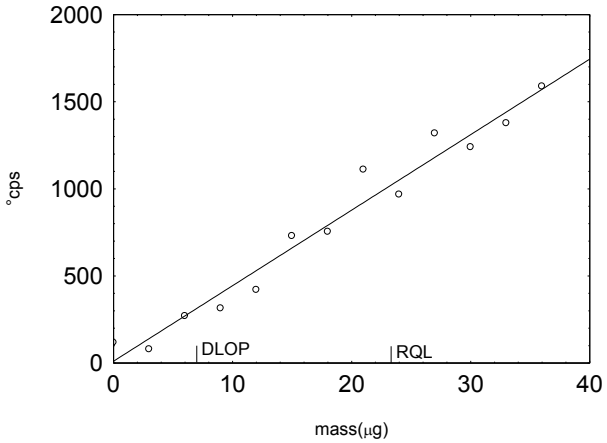

Figure 4.1.11. Example plot of data to determine the DLOP/RQL for cristobalite on the tertiary diffraction angle y = 43.4x + 10.6 (sample set 2).

Table 4.1.23
Detection Limit of the Overall Procedure for Cristobalite

sample set	mass /sample (µg)	primary angle (°cps)	secondary angle (°cps)	tertiary angle (°cps)	sample set	mass /sample (µg)	primary angle (°cps)	secondary angle (°cps)	tertiary angle (°cps)
1	0	54	23	16	4	0	78	30	82
1	3	955	49	30	4	3	875	43	79
1	6	1509	70	225	4	6	1588	85	166
1	9	2378	307	321	4	9	2327	181	265
1	12	3834	509	405	4	12	3068	486	438
1	15	4564	472	603	4	15	4525	519	526
1	18	5809	910	959	4	18	6178	728	801
1	21	7981	1039	1069	4	21	7305	1055	980
1	24	7374	1110	1060	4	24	6738	872	858
1	27	9074	1201	1326	4	27	7671	1006	1082
1	30	8702	1393	1245	4	30	9149	1288	1231
1	33	9893	1429	1656	4	33	8609	1265	1484
1	36	11026	1660	1787	4	36	9928	1457	1621
2	0	93	4	118	5	0	119	3	6
2	3	829	28	79	5	3	959	17	177
2	6	1980	117	270	5	6	1747	112	347
2	9	2384	294	314	5	9	2629	254	50
2	12	2908	390	420	5	12	4371	295	344
2	15	4238	326	729	5	15	5395	598	724
2	18	5151	563	754	5	18	6415	801	1126
2	21	6935	931	1110	5	21	5707	919	849
2	24	7840	1040	967	5	24	7371	1111	1012
2	27	9016	1066	1318	5	27	9243	1237	1429
2	30	8096	1216	1239	5	30	10713	1474	1776
2	33	8518	1395	1377	5	33	9836	1627	1795
2	36	10874	1703	1588	5	36	11961	1755	1829
3	0	77	50	6	6	0	58	0	33
3	3	1024	76	153	6	3	1048	31	101
3	6	1791	133	260	6	6	1597	80	196
3	9	2597	279	338	6	9	2299	222	257
3	12	4143	437	586	6	12	3482	436	437
3	15	5319	606	662	6	15	5161	608	609
3	18	5454	717	1130	6	18	5656	773	728
3	21	6370	650	1175	6	21	7595	1015	1033
3	24	8285	1106	999	6	24	7360	913	1012
3	27	9400	1214	1272	6	27	7248	1035	1002
3	30	10736	1753	1532	6	30	8510	1216	1290
3	33	10610	1448	1621	6	33	8570	1312	1233
3	36	10545	1664	1822	6	36	9925	1414	1592

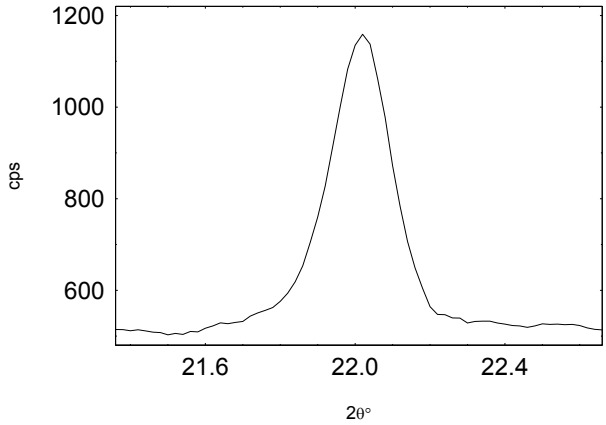

Figure 4.1.12. Scan of cristobalite at the RQL of the primary angle.

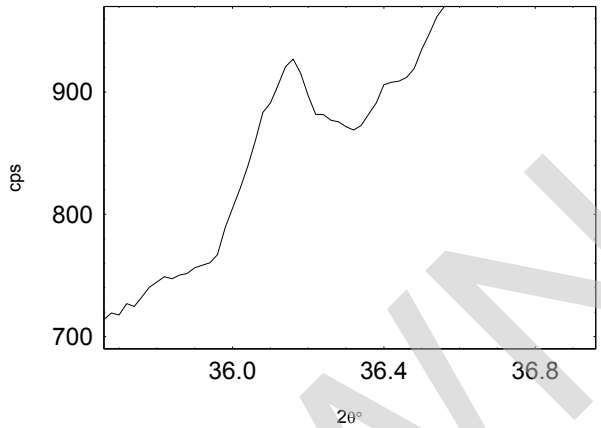

Figure 4.1.13. Scan of cristobalite at the RQL of the secondary angle.

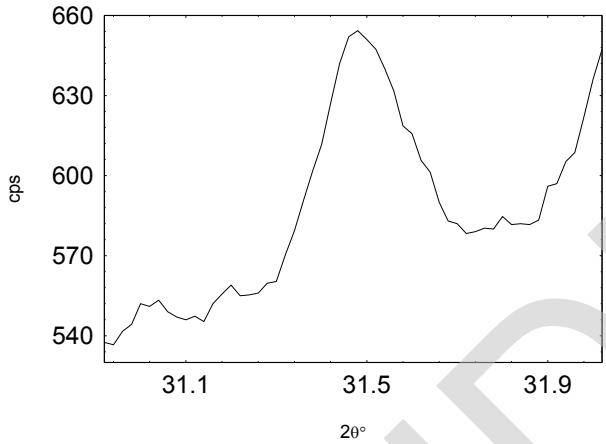

Figure 4.1.14. Scan of cristobalite at the RQL of the tertiary angle.

4.2 Precision (overall procedure)

The precision of the overall procedure at the 95% confidence level is obtained by multiplying the overall standard error of estimate by 1.96 (the z-statistic from the standard normal distribution at the 95% confidence level). The precision of the overall procedure at the 95% confidence level for quartz using the primary diffraction angle at the target concentration is ±16.0%. The precision of the overall procedure at the 95% confidence level for cristobalite using the primary diffraction angle at the target concentration is ±18.8%. These percentages contain an additional 5% sample pump error. The following data represents the analysis of silver membranes (10 at each level) with liquid deposition of 21.00 and 40.56 µg (25.74 and 49.71 µg/m^3) of quartz from NIST SRM 1878a quartz and with 20.00 and 40.00 µg (24.51 and 49.02 µg/m^3) of cristobalite from NIST SRM 1879a cristobalite. Table 4.2.1 shows the data used in the calculation of the precision for quartz. Table 4.2.2 shows the data used in the calculation of the precision for cristobalite.

Table 4.2.1
Precision Data for Quartz

	primary angle	secondary angle	tertiary angle	quaternary angle	primary angle	secondary angle	tertiary angle	quaternary angle
theoretical weight (µg)	21.00	21.00	21.00	21.00	40.56	40.56	40.56	40.56
sample 1	16.83	16.94	19.50	21.12	37.18	39.85	38.24	40.92
sample 2	20.11	18.53	21.29	20.38	40.08	42.49	38.81	38.69
sample 3	21.14	20.21	19.19	19.12	40.26	37.80	37.94	41.23
sample 4	20.31	20.33	20.23	21.38	35.02	36.74	37.54	36.40
sample 5	18.60	18.54	19.83	19.45	36.53	34.27	40.23	41.09
sample 6	19.78	17.31	20.17	18.75	39.20	40.49	38.10	41.72
sample 7	16.75	17.64	17.38	17.83	42.56	42.84	42.89	42.56
sample 8	17.28	15.07	17.57	18.25	35.81	36.80	34.90	35.27
sample 9	18.68	18.19	19.79	18.90	35.87	37.13	37.81	37.28
sample 10	17.36	17.94	18.73	20.59	36.88	36.38	40.76	39.89
mean (µg)	18.68	18.07	19.37	19.58	37.94	38.48	38.72	39.51
s	1.59	1.53	1.21	1.22	2.45	2.81	2.16	2.47
RSD (%)	8.5	8.5	6.2	6.3	6.5	7.3	5.6	6.3
SEE (%)	9.9	9.9	8.0	8.0	8.2	8.9	7.5	8.0
precision (%)	19.4	19.3	15.7	15.7	16.0	17.4	14.7	15.7
recovery (%)	89.0	86.0	92.2	93.2	93.5	94.9	95.5	97.4

Table 4.2.2
Precision Data for Cristobalite

	primary angle	secondary angle	tertiary angle	primary angle	secondary angle	tertiary angle
theoretical weight (µg)	20.00	20.00	20.00	40.00	40.00	40.00
sample 1	18.67	19.31	17.92	40.53	36.13	36.33
sample 2	18.88	19.39	19.29	32.31	32.14	33.45
sample 3	22.54	20.73	20.15	39.74	36.72	35.82
sample 4	18.83	17.63	15.63	37.44	35.65	34.66
sample 5	22.03	18.80	18.66	44.92	37.79	41.62
sample 6	17.70	17.17	16.20	38.19	35.74	33.51
sample 7	21.25	22.65	18.83	40.08	36.09	41.56
sample 8	19.00	16.97	18.66	39.03	38.62	31.27
sample 9	20.09	19.08	17.62	37.05	32.45	30.34
sample 10	21.09	16.12	19.73	40.10	34.85	39.44
mean (µg)	20.01	18.79	18.27	38.94	35.62	35.80
s	1.63	1.94	1.46	3.20	2.06	3.99
RSD (%)	8.2	10.3	8.0	8.2	5.8	11.1
SEE (%)	9.6	11.5	9.4	9.6	7.6	12.2
precision (%)	18.8	22.5	18.5	18.8	15.0	23.9
recovery (%)	100	93.9	91.3	97.3	89.0	89.5

4.3 Reproducibility

Six separate samples each were prepared for both quartz and cristobalite by liquid deposition of the analytes on PVC filters. The samples were submitted to the OSHA SLTC for analysis and analyzed. No sample result for crystalline silica had a deviation greater than the precision of the overall procedure reported in Section 4.2. The data are shown in Tables 4.3.1 and 4.3.2.

Table 4.3.1
Reproducibility Data for Quartz

	primary angle		secondary angle		tertiary angle		quaternary angle	
theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	recovered (µg/sample	recovery (%)	recovered (µg/sample)	recovery (%)	recovered (µg/sample	recovery (%)
40.0	41.84	105	38.51	96.3	42.20	106	41.84	105
40.0	43.70	109	43.02	108	39.66	99.2	39.45	98.6
40.0	44.72	112	43.93	110	43.25	108	46.10	115
40.0	41.22	103	42.27	106	43.13	108	39.55	98.9
40.0	38.50	96.3	35.58	89.0	41.10	103	34.54	86.4
40.0	38.78	97.0	37.17	92.9	36.25	90.6	42.12	105

Table 4.3.2
Reproducibility Data for Cristobalite

	primary angle		secondary angle		tertiary angle	
theoretical (µg/sample)	recovered (µg/sample)	recovery (%)	recovered (µg/sample)	recovery (%)	recovered (µg/sample)	recovery (%)
40.0	39.44	98.6	38.60	96.5	42.47	106
40.0	37.22	93.1	40.25	101	39.67	99.2
40.0	39.74	99.4	38.10	95.3	43.64	109
40.0	36.87	92.2	36.37	90.9	35.18	88.0
40.0	42.62	107	40.26	101	42.75	107
40.0	44.06	110	37.27	93.2	46.58	117

4.4 Cowl wiping procedure

To determine the efficacy of the cowl wiping procedure described in 3.4.1, compliance samples with varying dust weights were selected and analyzed for quartz according to the procedure described in this method. Samples were selected because visual observation confirmed the presence of dust on the cowl, or because of high dust weights. The aluminum cowls of these samples were then wiped a second time to ensure that no quartz remained. Some of the samples contained no detectable amount of silica and were excluded from the study. The 49 samples that remained had an average dust weight of 1464 µg.

The results of these second wipes are summarized in Table 4.4. Of the 49 second wipes that were analyzed seven had amounts of quartz on the membrane that were above the DLOP, but less than the RQL of the method. Two second wipes had measurable amounts of quartz greater than the RQL. The two wipes that contained quantifiable amounts of quartz were associated with samples that had weights of 1886 and 2069 µg. Analysis of the silver membranes for these samples showed that they contained 896 and 923 µg quartz. The amount of quartz found on the second wipe samples were 15 and 30 µg respectively. This represents 1.7 and 3.3% of the total quartz present, and missed by the single cowl wiping procedure described in this method. Samples with results near the target concentration (40 µg/sample) of this method do not show any traces of quartz left after the first wipe. The data confirms the efficacy of a single cowl wiping procedure described in Section 3.4.1.

Table 4.4
Summary Results of Second Wipe

µg quartz in sample	number of samples	silica present on wipe but less than RQL	silica present on wipe greater than RQL
0-80 µg	10	0	0
80-130 µg	10	2	0
130-215 µg	10	0	0
215-355 µg	10	2	0
355-760 µg	7	3	0
>760 µg	2	0	2

Appendix A
Interference Acid Digestion Procedure

In the absence of confirming peaks attempt to remove interferences through acid digestion using this procedure. Subject spiked samples of known quantity and a blank sample to the procedure as control samples.

A.1 Apparatus

A closed vessel microwave digestion system. A CEM Discover SP-D system equipped with activent pressure control and an auto-sampler with CEM synergy-D v1.10 control software was used in this validation.

Digestion Vessels. CEM 35-mL Pyrex digestion vessels (catalog no. 909036) were used in this validation.

Digestion vessel caps. CEM 35-mL digestion vessel snap-on caps with Teflon liners (catalog no. 909350) were used in this validation.

Small magnetic stir bars. VWR 10 x 3 mm Teflon micro stir bars (catalog no. 47744-998) were used in this validation.

PVC filters. SKC Inc. 5-µm pore size 47-mm (catalog no. 225-5-47) PVC filters were used in this validation.

Drying oven. A Sheldon Mfg. Co. Model 1480, vacuum oven was used in this validation.

Large magnetic stir bar.

Büchner funnel and side arm flask vacuum filtering apparatus designed to accommodate 47-mm filters.

Dispenser bottles, 8.5 mL for phosphoric acid, 2.5 mL for nitric acid.

Centrifuge tubes, glass round bottom 50-mL, with rack to hold tubes.

Dropping bottles with eyedroppers for fluoroboric acid.

Tweezers.

A.2 Reagents

All reagents should be reagent grade or better.

Nitric acid, [CAS no. 7697-37-2]. The nitric acid used in this validation was 69-70% pure (lot no. 0000088969) purchased from JT Baker.

Phosphoric acid, [CAS no. 7664-38-2]. The phosphoric acid used in this validation was ≥85% pure (lot no. 142201) purchased from Fisher Scientific.

Fluoroboric acid, [CAS no. 16872-11-0]. The fluoroboric acid (tetrafluoroboric acid used in this validation was 48-50% pure (lot no. 137152) purchased from Fisher Scientific.

Dionized water, 18.0 MΩ-cm, a Barnstead NANOpure Diamond water purification system was used in this validation.

A.3 Procedure

Place the silver membrane inside a 35-mL Pyrex digestion vessel along with a small magnetic stir bar. Add 8.5 mL of phosphoric acid, followed by 2.5 mL of nitric acid. Ensure the silver membrane is completely immersed in the acid. Cap the vessel with a Teflon-lined cap and immediately microwave the vessel to accomplish the digestion of the interferences and the silver membrane.

The digestion takes place with medium speed stirring (570 rotations per minute). The acid mixture inside the vessel is microwave heated to a temperature of 130 °C over a period of 6.5 minutes. The temperature is then held at 130 °C for 20.0 minutes. The pressure is set to vent at 200 psi so the vessel cannot exceed this pressure. The maximum power setting is 200 W. Once the digestion is complete, the microwave system rapidly cools the vessel to 80 °C. When the digestion and cooling are complete, remove the vessel from the microwave.

Place a 47-mm, 5.0-µm pore size PVC filter on the vacuum filtering apparatus and turn on the vacuum. Immediately after digestion, transfer the solution to the filtering apparatus and let the solution begin to pass through the filter. With the digestion vessel held at about a 45° angle, use a squirt bottle containing deionized water to quantitatively rinse any remaining sample into the vacuum filtering apparatus. Digested interferences pass through the PVC filter, while the crystalline silica remains on the PVC filter.

Rinse the digestion vessel with a small amount of fluoroboric acid and transfer it to the filtering apparatus. Following the fluoroboric acid rinse, rinse the vessel again with deionized water.

Use a large magnetic stir bar to retrieve the small magnetic stir bar from the apparatus. Rinse the small stir bar with a small amount of fluoroboric acid and transfer it to the filtering apparatus. Following the fluoroboric acid rinse, rinse the small stir bar again with deionized water.

Rinse down the walls of the filtering apparatus with a small amount of fluoroboric acid. Following the fluoroboric acid rinse, rinse the walls again with deionized water.

Once the PVC filter is visibly dry, carefully fold the filter into quarters with the sample inside. Carefully place the folded filter into an individual centrifuge tube.

Dry the filter in a vacuum oven at 40 °C for 1 hr.

Re-dissolve the filters in THF and re-deposit the suspended sample on a silver membrane for analysis as described in Section 3.4.1.

A.4 Validation data

In order to test this acid digestion procedure, three silver membranes were spiked with 40 µg of quartz and three other silver membranes were spiked with 40 µg of cristobalite. Each of the membranes were then spiked with 2000 µg of kaolinite ($Al_2Si_2O_5(OH)_4$) which had been previously sized to less than 10 µm using a sonic sifter. Kaolinite was chosen because it was shown to interfere on multiple diffraction angles that are used to analyze both quartz and cristobalite. The kaolinite used in this validation was Kaolinite China Clay – powdered (lot no. 46E0995) obtained from Ward's Natural Science Est. Incorporated.

The silver membranes were analyzed for quartz or cristobalite by XRD as described in Section 3.5.2. The silver membranes were subjected to the acid digestion procedure described in this appendix. The resulting dry PVC filters were then re-dissolved in THF and the samples were re-deposited on new silver membranes for analysis by XRD.

The results obtained for the silver membranes before and after the acid digestion procedure are shown in Tables A.4.1 and A.4.2. Figures A.4.1 through A.4.14 are scans of the analytical angles of quartz and cristobalite before and after the acid digestion procedure.

Table A.4.1
Quartz Recoveries (µg) Before and After Acid Digestion

	before				after			
	primary angle	secondary angle	tertiary angle	quaternary angle	primary angle	secondary angle	tertiary angle	quaternary angle
sample 1	50.24	30.26	39.59	324.53	56.55	38.64	40.24	44.99
sample 2	58.77	37.69	55.62	386.77	47.28	40.05	41.71	44.77
sample 3	58.72	39.67	50.59	372.45	44.80	42.52	41.16	38.46

Table A.4.2
Cristobalite Recoveries (µg) Before and After Acid Digestion

	before			after		
	primary angle	secondary angle	tertiary angle	primary angle	secondary angle	tertiary angle
sample 1	48.97	584.79	50.74	40.99	43.12	34.34
sample 2	51.43	624.67	53.48	39.75	43.87	33.19
sample 3	52.43	636.37	54.03	38.22	43.47	37.60

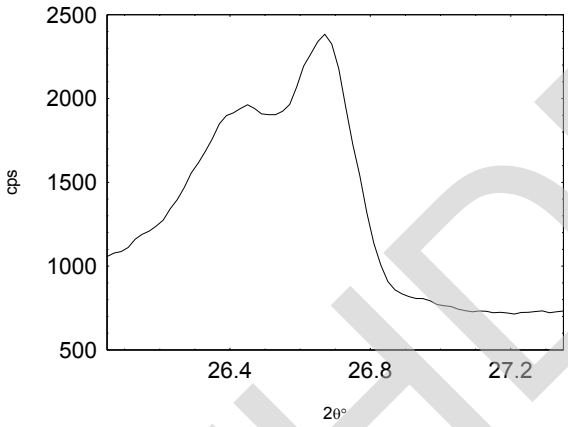

Figure A.4.1. Scan of primary quartz angle before acid digestion procedure.

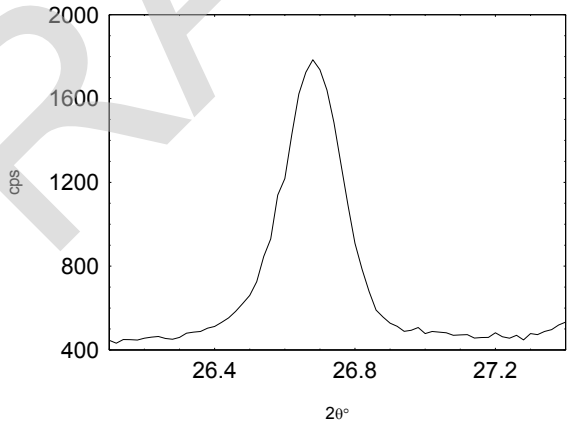

Figure A.4.2. Scan of primary quartz angle after acid digestion procedure.

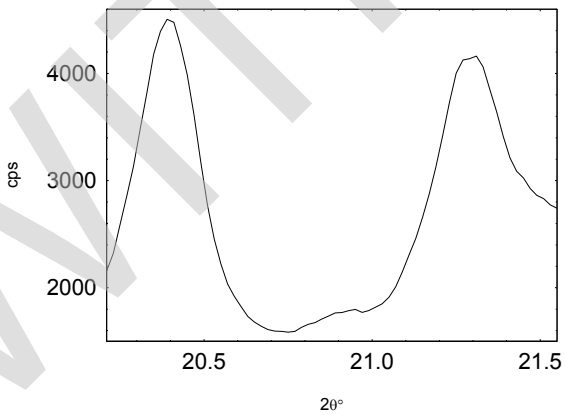

Figure A.4.3. Scan of secondary quartz angle before acid digestion procedure.

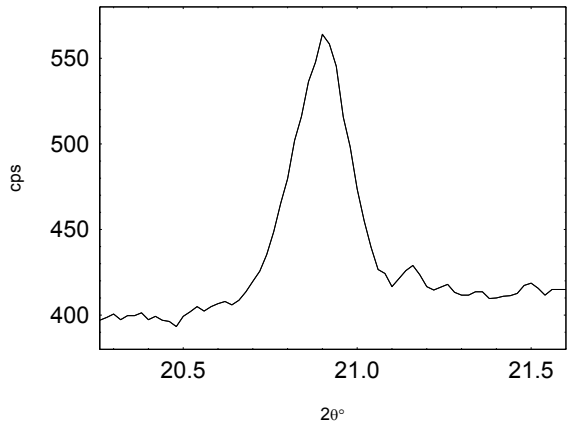

Figure A.4.4. Scan of secondary quartz angle after acid digestion procedure.

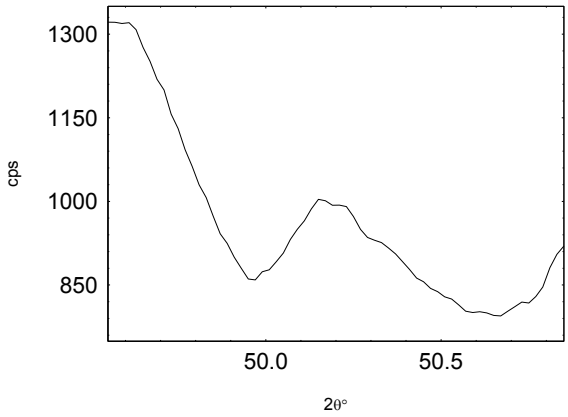

Figure A.4.5. Scan of tertiary quartz angle before acid digestion procedure.

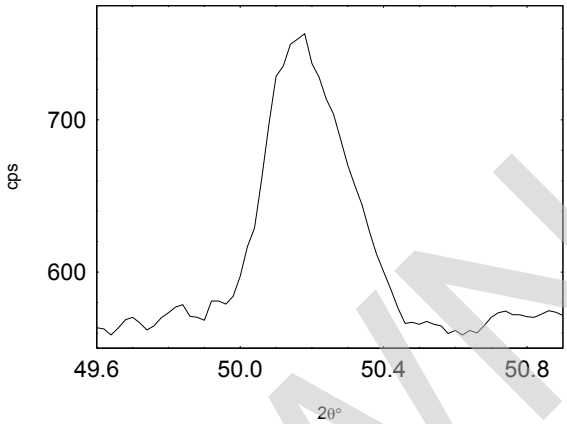

Figure A.4.6. Scan of tertiary quartz angle after acid digestion procedure.

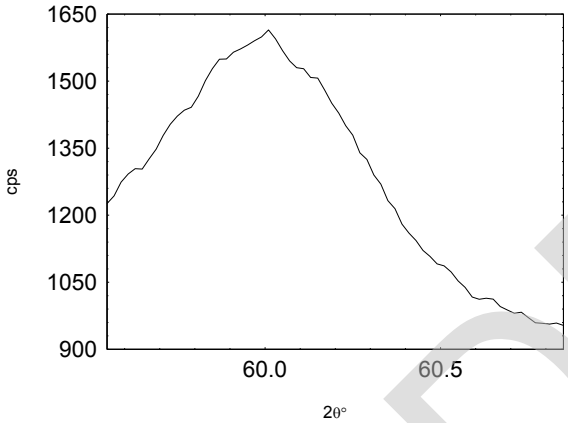

Figure A.4.7. Scan of quaternary quartz angle before acid digestion procedure.

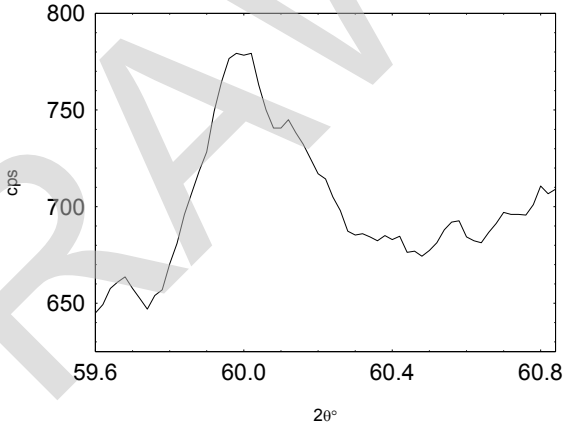

Figure A.4.8. Scan of quaternary quartz angle after acid digestion procedure.

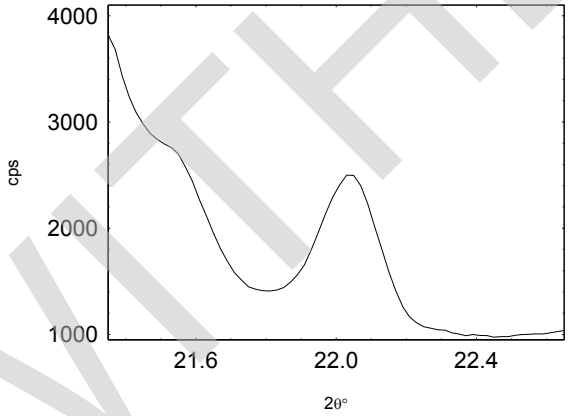

Figure A.4.9. Scan of primary cristobalite angle before acid digestion procedure.

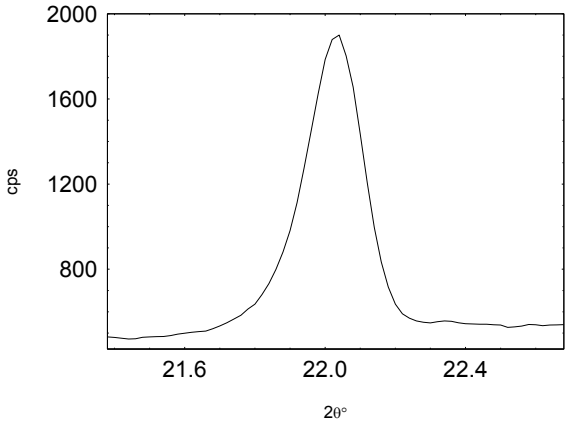

Figure A.4.10. Scan of primary cristobalite angle after acid digestion procedure.

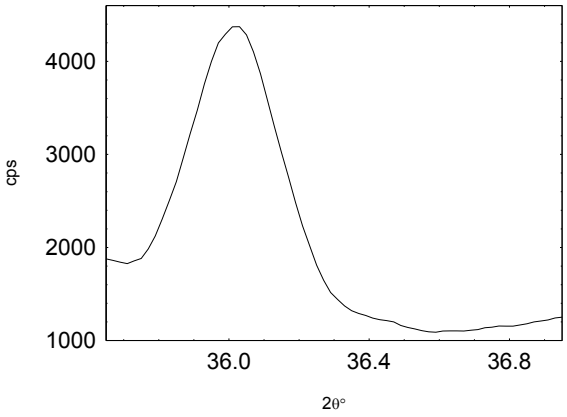

Figure A.4.11. Scan of secondary cristobalite angle before acid digestion procedure.

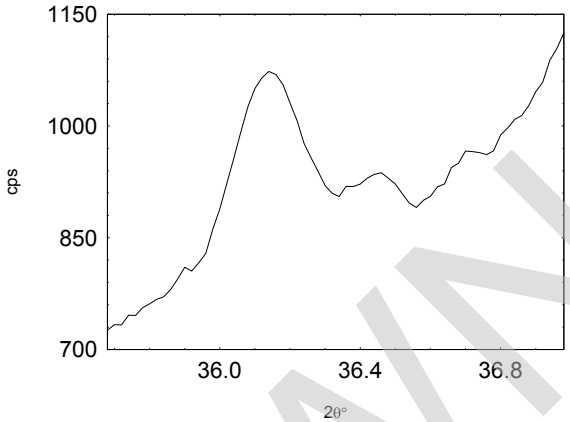

Figure A.4.12. Scan of secondary cristobalite angle after acid digestion procedure.

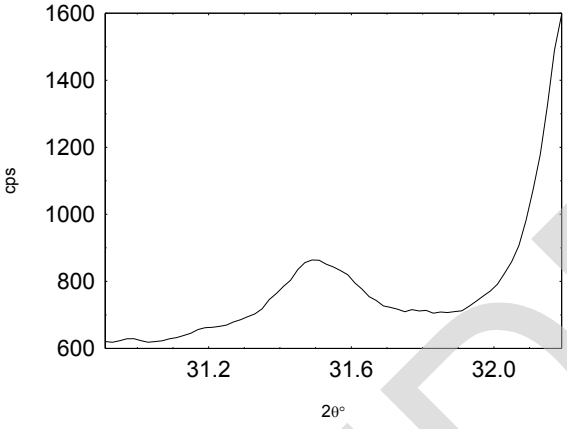

Figure A.4.13. Scan of tertiary cristobalite angle before acid digestion procedure.

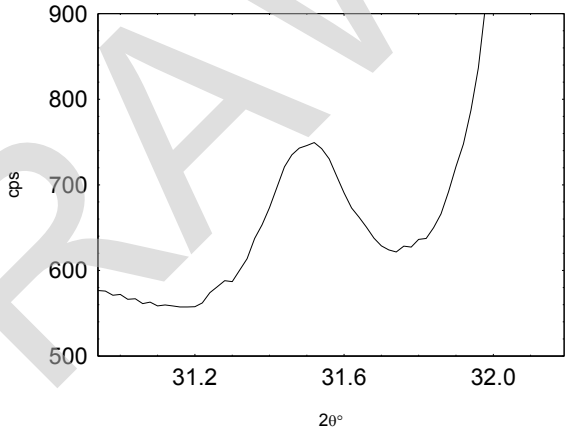

Figure A.4.14. Scan of tertiary cristobalite angle after acid digestion procedure.

The quartz results obtained before the acid digestion procedure demonstrate significant interference, especially on the quaternary peak. There are no confirming peak results in the samples. Obvious multiple peaks and shoulder peaks are affecting the integration. After the acid wash procedure is used to remove the kaolinite from the samples, quartz results show better agreement. For quartz samples 2 and 3 all other peak results confirm the lowest peak result, and all peaks appear free of interference. All peaks are averaged for the results. For quartz sample 1 the tertiary and quaternary peaks confirm the secondary peak. These three peaks appear free of interference, so they are averaged for the result. The results for quartz are 41.3, 43.5, and 41.7 µg/sample. These results give recoveries of 103%, 109%, and 104%.

The cristobalite results obtained prior to the acid digestion procedure demonstrate significant interference, especially on the secondary peak. There are no confirming peak results in the samples. Even where the results mathematically confirm, obvious multiple peaks and shoulder peaks are affecting the integration. After the acid wash procedure is used to remove the kaolinite from the samples, cristobalite results show better agreement. For cristobalite sample 3 both other peak results confirm the lowest peak result, and all peaks appear free of interference. All peaks are averaged for the results. For cristobalite samples 1 and 2 the primary peak confirms the tertiary peak. Both these peaks appear free of interference, so they are averaged for the result. The results for cristobalite are 37.7, 36.5, and 39.8 µg/sample. These results give recoveries of 94.2%, 91.2%, and 99.5%.

Appendix B
Analytical Interferences

The majority of the interferences listed below in Tables B.1 through B.6 will most likely not be present when sampling industrial operations which produce quartz or cristobalite exposures. This list is presented as angle-matches found in the 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 angles of that substance have a peak within ±0.65° 2θ of the specific analyte angles. PDF No. = JCPDS Powder Diffraction File Number

Table B.1
Potential Interferences-Primary Quartz Angle

Interferent	Formula	PDF No.
Aluminum Phosphate (Berlinite)	$AlPO_4$	10-423
Biotite	$K(Fe,Mg)_3\ AlSi_3O_{10}(OH)_3$	2-45
Clinoferrosilite	$FeSiO_3$	17-548
Graphite	C	23-064,
High Albite	$NaAlSi_3O_8$	20-572
Iron Carbide	FeC	3-411
Kaolinite	$Al_2Si_2O_5(OH)_4$	14-164
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	$KMgAlSi_4O_{10}(OH)_2$ $KAl_2Si_3AlO_{10}(OH)_2$ $KAl_2(Si_3Al)O_{10}(OH,F)_2$ $K(Al,V)_2(Si,Al)_4O_{10}(OH)_2$ $(K,Na)Al_2(Si,Al)_4O_{10}(OH)_2$ $(Ba,K)Al_2(Si_3AlO_{10})(OH)_2$ $(K,Ca,Na)(Al,Mg,Fe)_2(Si,Al)_4O_{10}(OH)_2$ $(K,Na)(Al,Mg,Fe)_2(Si_{3.1}Al_{0.9})O_{10}(OH)_2$	21-993 7-25 6-263 19-814 34-175 10-490 25-649 7-42
Orthoclase	$KAlSi_3O_8$ $(K,Ba)(Si,Al)_4O_8$ $(K,Ba,Na)(Si,Al)_4O_8$	31-966 19-3 19-2
Potassium Hydroxide	KOH	15-890
Sanidine	$(K,Na)AlSi_3O_8$ $KAlSi_3O_8$	19-1227 25-618
Sillimanite	Al_2SiO_5	38-471
Wollastonite	$CaSiO_3$ $(Ca,Fe)SiO_3$	27-1064, 10-489, 27-88 27-1056
Zircon	$ZrSiO_4$	6-266

Table B.2
Potential Interferences-Secondary Quartz Angle

Interferent	Formula	PDF No.
Aluminum Phosphate (Berlinite)	$AlPO_4$	10-423
High Albite	$NaAlSi_3O_8$	20-572
Kaolinite	$Al_2Si_2O_5(OH)_4$	14-164
Microcline	$KAlSi_3O_8$	19-932, 22-675, 22-687, 19-926

Table B.3
Potential Interferences-Tertiary Quartz Angle

Interferent	Formula	PDF No.
Aluminum Phosphate (Berlinite)	$AlPO_4$	10-423
Copper	Cu	4-836

Table B.4
Potential Interferences-Primary Cristobalite Angle

Interferent	Formula	PDF No.
Aluminum Phosphate	$AlPO_4$	11-500
High Albite	$NaAlSi_3O_8$	10-393, 20-572

Table B.5
Potential Interferences- Secondary Cristobalite Angle

Interferent	Formula	PDF No.
Aluminum Phosphate (Aluminum Phosphate Berlinite)	$AlPO_4$	11-500, 10-423
High Albite	$NaAlSi_3O_8$	10-393, 20-572
Kaolinite	$Al_2Si_2O_5(OH)_4$	14-164
Quartz	SiO_2	33-1161

Table B.6
Potential Interferences-Tertiary Cristobalite Angle

Interferent	Formula	PDF No.
Aluminum Phosphate	$AlPO_4$	11-500