

SILICA, CRYSTALLINE, by XRD (filter redeposition)

7500

SiO₂ MW: 60.08 CAS: 14808-60-7 (quartz) RTECS: VV7330000 (quartz)
 14464-46-1 (cristobalite) VV7325000 (cristobalite)
 15468-32-3 (tridymite) VV7335000 (tridymite)

METHOD: 7500, Issue 4

EVALUATION: FULL

Issue 1: 15 August 1990

Issue 4: 15 March 2003

OSHA: quartz (respirable) 10 mg/m³/(%SiO₂+2);
 cristobalite and tridymite (respirable) ½ the above
NIOSH: 0.05 mg/m³; carcinogen
ACGIH: quartz (respirable) 0.1 mg/m³
 cristobalite (respirable) 0.05 mg/m³
 tridymite (respirable) 0.05 mg/m³

PROPERTIES: solid; d 2.65 g/cm³ @ 0 °C; crystalline
 transformations: quartz to tridymite
 @ 867 °C; tridymite to cristobalite @ 1470
 °C; α-quartz to β-quartz @ 573 °C

SYNONYMS: free crystalline silica; silicon dioxide

| SAMPLING | | MEASUREMENT | |
|---|--|-----------------------------------|---|
| SAMPLER: | CYCLONE + FILTER (10-mm nylon cyclone, Higgins-Dewell (HD) cyclone, or aluminum cyclone + 5-µm PVC membrane) *see sampling section | TECHNIQUE: | X-RAY POWDER DIFFRACTION |
| FLOW RATE: | Nylon cyclone: 1.7 L/min; HD cyclone: 2.2 L/min; aluminum cyclone: 2.5 L/min | ANALYTE: | Crystalline SiO ₂ |
| VOL-MIN: | 400 L | ASH: | Muffle furnace or RF plasma asher or dissolve in tetrahydrofuran |
| -MAX: | 1000 L | REDEPOSIT: | On 0.45-µm Ag membrane filter |
| SHIPMENT: | Routine | XRD: | Cu target X-ray tube, graphite monochromator Optimize for intensity; 1° slit Slow step scan, 0.02°/10 sec Integrated intensity with background subtraction |
| SAMPLE STABILITY: | Stable | CALIBRATION: | NIST SRM 1878a quartz, NIST SRM 1879a cristobalite, USGS 210-75-0043 tridymite suspensions in 2-propanol. |
| BLANKS: | 2 to 10 per set (see step 13.g.) | RANGE: | 0.02 to 2 mg SiO ₂ per sample [2] |
| BULK SAMPLE: | High-volume or settled dust; to identify interferences | ESTIMATED LOD: | 0.005 mg SiO ₂ per sample [2] |
| ACCURACY | | PRECISION (Ŝ_r): | 0.08 @ 0.05 to 0.2 mg per sample [1] |
| RANGE STUDIED: | 25 to 2500 µg/m ³ [1] (800-L sample) | | |
| BIAS: | None known | | |
| OVERALL PRECISION (Ŝ_{r,T}): | 0.09 (50 to 200 µg) [1] | | |
| ACCURACY: | ± 18% | | |

APPLICABILITY: The working range is 0.025 to 2.5 mg/m³ for an 800-L air sample.

INTERFERENCES: Micas, potash, feldspars, zircon, graphite, and aluminosilicates. See APPENDIX.

OTHER METHODS: This is similar to the method in the Criteria Document [3] and P&CAM 259 [4] which has been collaboratively tested [1]. This method is similar, except for sample collection, to S315 [5,6]. Method P&CAM 109 [7,8,9], which incorporates an internal standard, has been dropped. XRD can distinguish the three silica polymorphs and silica interferences can be eliminated by phosphoric acid treatment. IR (methods 7602 and 7603) can also quantify quartz, cristobalite and tridymite if amorphous silica and silicates are not present in large amounts. However sensitivity is reduced if multiple polymorphs are present and secondary peaks must be used. Crystalline silica can also be determined by visible absorption spectrophotometry (e.g., Method 7601), but polymorphs can not be distinguished. Visible absorption methods also have larger laboratory-to-laboratory variability than XRD and IR methods and therefore are recommended for research use only [10].

REAGENTS:

1. Silica Standards.
 - a. Quartz* (SRMs 1878a, 2950, 2951, 2958) and Cristobalite* (SRMs 1879a, 2960, 2957), available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899; www.nist.gov.
 - b. Tridymite* (210-75-0043) available from U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225.
2. 2-Propanol*, reagent grade.
3. Desiccant.
4. Glue or tape for securing Ag filters to XRD holders.
5. Optional: tetrahydrofuran (THF)* (if LTA or muffle furnace are unavailable).
6. 1.5 % parlodion solution. (Dissolve 1.5 g of parlodion* in isopentyl acetate* and dilute to 100 mL with isopentyl acetate.)
7. Optional (if calcite present): 25% v/v concentrated hydrochloric acid* (ACS reagent grade) in distilled water and 25-mm filters of PVC or cellulose ester with pore size of 1 µm or less.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. Filter: Polyvinyl chloride (PVC) filter, 37-mm, 5.0-µm pore size supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
NOTE: Check each new lot of PVC filters by analyzing one or more by this method. For example, Gelman VM-1 filters (all lots) were found to be unacceptable because of high ash and background. If THF is used, check for complete dissolution by dissolving a blank PVC filter and following steps 5c through 8.
 - b. Cyclone: 10-mm nylon, Higgins-Dewell (HD), Aluminum (Al), or equivalent [11].
2. Area air sampler: PVC membrane filter, 37-mm diameter, 5-µm pore size; three-piece filter cassette.
3. Sampling pumps with flexible connecting tubing, capable of the following flow rates: nylon cyclone, 1.7 L/min; HD cyclone, 2.2 L/min; Al cyclone, 2.5 L/min; and bulk sampler, 3 L/min.
4. Silver membrane filters, 25-mm diameter, 0.45-µm pore size, available from Sterlitech Corp., 22027 70th Ave S, Kent, WA 98032-1911; www.sterlitech.com.
5. X-ray powder diffractometer (XRD) equipped with copper target X-ray tube, graphite monochromator, and scintillation detector.
6. Reference specimen (mica, Arkansas stone, or other stable standard) for data normalization.
7. Low-temperature radio-frequency plasma asher (LTA) or muffle furnace, or ultrasonic bath (≥ 150 W), for filter preparation.
8. Vacuum filtration assembly and side-arm vacuum flask with a 25-mm filter holder.
9. Sieve, 10-µm, for wet sieving.
10. Analytical balance (0.001 mg); magnetic stirrer with thermally insulated top; ultrasonic bath or probe; volumetric pipettes and flasks; Pyrex crucibles with covers (muffle furnace); 40-mL wide-mouth or 50-mL centrifuge tubes (THF method); desiccator; reagent bottles with ground glass stoppers; drying oven; polyethylene wash bottle.
11. Explosion-resistant hot plate.
12. Teflon sheet, 0.3 to 1 mm thick.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [3]. THF is extremely flammable and should be used in a fume hood. 2-Propanol, parlodion and isopentyl acetate are flammable. Hydrochloric acid is corrosive and should be used in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at $1.7 \pm 5\%$ L/min with nylon cyclone or $2.2 \pm 5\%$ L/min with HD cyclone for a total sample size of 400 to 1000 L. Do not exceed 2 mg dust loading on the filter.
NOTE 1: Do not allow the sampler assembly to be inverted at any time when using a cyclone. Turning the cyclone to anything other than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.
NOTE 2: A single sampler/flow rate should be used for a given application. Sampling for both crystalline silica and coal mine dust should be done in accordance with the ISO/CEN/ACGIH/ASTM respirable aerosol sampling convention. Flow rates of 1.7 L/min for the Dorr-Oliver nylon cyclone and 2.2 L/min for the Higgins-Dewell cyclone have been found to be optimal for this purpose. Outside of coal mine dust sampling, the regulatory agencies currently use these flow rates with the Dorr-Oliver cyclone in the United States and the Higgins-Dewell sampler in the United Kingdom. Though the sampling recommendations presented in a NIOSH Criteria Document have been formally accepted by MSHA for coal mine dust sampling, the Dorr-Oliver cyclone at 2.0 L/min with 1.38 conversion factor is currently used in the United States for the purpose of matching an earlier sampling convention [12]. In any case, a single sampler/flow rate should be used in any given application so as to eliminate bias introduced by differences between sampler types and sampler conventions [11].
3. Take an area air sample or collect a settled dust sample, if dust in the work environment has not been previously characterized.

SAMPLE PREPARATION:

4. Samples may be characterized by one of the following methods, as appropriate.
 - a. **Interference check.** Prepare area dust sample or settled dust bulk sample for XRD analysis by mounting the collection sample directly on an XRD sample holder, or by depositing or redepositing the dust on another filter for mounting, or by packing an XRD powder holder. Proceed to step 11.
 - b. **Qualitative Analysis.** Prepare the area air sample or settled dust sample for qualitative analysis by grinding and/or wet sieving to best match the airborne dust particle size. Wet sieve with a 10- μ m sieve, 2-propanol, and an ultrasonic bath [13], followed by evaporation of excess alcohol, drying in an oven for 2 hours, and overnight storage in a desiccator. Deposit the end product on a filter (steps 7-8) or pack in a conventional XRD powder holder.
NOTE 1: For quantitative determination of % SiO₂, weigh out, in triplicate, 2 mg sieved dust, transfer to a 50-mL beaker, add 10 mL 2-propanol, and continue with step 6.
NOTE 2: In a bulk sample, if there is an interfering compound(s) that renders the identification and quantitation of quartz very difficult, the sample will need to be carefully treated in hot phosphoric acid [14] to dissolve the interfering compound(s) and avoid the loss of quartz. This treatment can be used to dissolve several 50-mg sample aliquots in order to concentrate the quartz content for the purpose of lowering the LOD.
5. Use one of the following methods to prepare filter samples and blanks:
 - a. **Low Temperature Ashing:** Place the filters in 50-mL beakers within the low temperature asher so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, carefully add 15 mL 2-propanol to each beaker; or
 - b. **Muffle Furnace Ashing:**
 - i. If the samples contain a significant amount of calcite (>20% of total dust loading), silica may be lost due to formation of CaSiO₃. Remove the calcite by the following procedure: Place a 0.5- μ m, 25-mm PVC filter in the filtration apparatus and clamp the filter funnel over it. Remove the sample filter from the cassette, fold, and drop it on the 25-mm filter. Add 10 mL 25% v/v HCl and 5 mL 2-propanol to the filter funnel and allow to stand for 5 min. Apply vacuum and slowly aspirate the

- acid and alcohol in the funnel, washing with three successive 10-mL portions of distilled water. Release the vacuum. Carry both filters through the ashing step together.
- ii. Place the filter samples in porcelain crucibles, loosely cover and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL 2-propanol to the ash, scrape the crucible with a glass rod to loosen all particles and transfer the residue to a 50-mL beaker. Wash the crucible several more times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to about 15 mL; or
 - c. **Filter Dissolution:** Using forceps and a spatula, remove the filter from the cassette, fold the filter three times, and place in the bottom of a 40- or 50-mL centrifuge tube. Add 10 mL THF and allow to stand for at least 5 min. Cap the centrifuge tube with aluminum foil to prevent contamination. Gently agitate the centrifuge tube by hand or with a vortex mixer making sure the THF does not go near the top of the tube. Place the tube in an ultrasonic bath (water level 2.5 cm from top) for at least 10 min. (The filter should be totally dissolved.) Just prior to filtering, agitate the sample for 10 to 20 sec on a vortex mixer. Continue with step 6, substituting THF for 2-propanol and centrifuge tube for beaker.
6. Cover the beaker with a watchglass and agitate in an ultrasonic bath for at least 3 min. Observe the suspension to make sure that the agglomerated particles are broken up. Wash the underside of the watchglass with 2-propanol, collecting the washings in the beaker.
 7. Place a silver filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL 2-propanol onto the filter. Pour the sample suspension from the beaker into the funnel. After the transfer, rinse the beaker several times and add rinsings to the funnel for a total volume of 20 mL. In order to minimize feathering of the sample outside the deposition area, allow the suspension to settle for a few minutes prior to applying vacuum. Do not rinse the chimney after the material has been deposited on the silver filter. Rinsing the chimney can disturb the thin layer deposition.
 8. Leave the vacuum on after filtration to produce a dry filter. Place 2 drops of 1.5% parlodion solution on a glass slide. Remove the silver filter with forceps and fix the material to the filter by placing the bottom side of the filter in the parlodion solution. Place the saturated filter on top of the Teflon sheet which has been heated on the hot plate at a low temperature setting. When thoroughly dry, mount the silver filter in the XRD sample holder.

CALIBRATION AND QUALITY CONTROL:

9. Prepare and analyze at least 6 levels of standard filters.
 - NOTE 1: Calibration standards are limited to NIST and USGS certified standards of known purity, particle size, and sample-to-sample homogeneity. At least 12 materials, including 5- μ m Min-U-Sil, previously used by laboratories throughout the United States and Canada, have been evaluated, and none have been found to be acceptable alternatives to the certified standards cited within this method [10]. Standard reference materials should be corrected for phase purity.
 - NOTE 2: Crystalline silica methods require calibration standards of known purity, specific particle size and distribution, and sample-to-sample homogeneity. Establishing traceability of secondary calibration standards to the specified NIST and USGS primary standards requires the use of measurement methods with better precision and accuracy than the XRD, IR and visible absorption spectrophotometry methods commonly used in the industrial hygiene field can provide. In addition, particle size distribution measurements have considerable error. Therefore, the use of secondary calibration standards that are traceable to NIST and USGS certified standards is not appropriate.
 - NOTE 3: NIST SRM 2950 calibration set (α -quartz) and NIST SRM 2960 calibration set (cristobalite) may be useful for preparing working standards at known concentrations.
- a. Prepare two suspensions of each analyte in 2-propanol by weighing 10 and 50 mg of the standard material to the nearest 0.01 mg. Quantitatively transfer each to a 1-L glass-stoppered bottle using 1.00 L of 2-propanol.
- b. Suspend the powder in 2-propanol with an ultrasonic probe or bath for 20 min. Immediately move the bottle to a magnetic stirrer with thermally insulated top and add a stirring bar. Allow the solution to return to room temperature before withdrawing aliquots.

- c. Mount a silver filter on the filtration apparatus. Place several mL of 2-propanol on the filter. Turn off the stirrer and shake vigorously by hand. Immediately remove the stopper and withdraw an aliquot from the center at half-height of the 10 mg/L or 50 mg/L suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the silver filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
- d. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several times.
- e. Allow the suspension to settle for a few minutes prior to applying vacuum. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposit is in place since this will rearrange the material on the silver filter. Leave vacuum on until filter is dry. Place 2 drops of 1.5% parlodion solution on a glass slide. Remove the silver filter with forceps and fix the material to the filter by placing the bottom side of the filter in the parlodion solution. Place the saturated filter on top of the heated Teflon sheet. When thoroughly dry, mount the silver filter in the XRD sample holder. Prepare working standard filters, in triplicate, at e.g., 10, 20, 50, 100, 250, and 500 μg .
- f. Analyze the working standards together with samples and blanks (step 12). The XRD intensities for the working standards (step 12.d) are designated I_x^0 and are then normalized (step 12.e) to obtain \hat{I}_x^0 . Correct the intensities of working standards $>200 \mu\text{g}$ for matrix absorption (steps 12.f and 13).
- g. Prepare a calibration graph (\hat{I}_x^0 , vs μg of each standard).
NOTE: Poor repeatability ($>10\%$ above 0.04 mg silica) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/\sigma^2$ weighting) is preferable.
- h. Determine the slope, m , of the calibration graph in counts/ μg . The intercept, b , on the abscissa should be within $\pm 5 \mu\text{g}$ of zero.
NOTE: A large intercept indicates an error in determining the background, i.e., an incorrect baseline or interference by another phase.
10. NOTE: The following procedure for absorption correction is not necessary in situations that have been previously documented as requiring no corrections.
Select six silver membrane filters as media blanks randomly from the same box of filters to be used for depositing the samples. These will be used to test for sample self-absorption. Mount each of the media blanks on the filtration apparatus and apply vacuum to draw 5 to 10 mL 2-propanol through the filter. Remove, let dry, and mount on XRD holders. Determine the net normalized count for the silver peak, \hat{I}_{Ag} , for each media blank (step 12.g). Obtain an average value for the six media blanks, \hat{I}_{Ag}^0 .
- NOTE: The analyst is a critical part of this analytical procedure [12]. A high level of analyst expertise is required to optimize instrument parameters and correct for matrix interferences either during the sample preparation phase or the data analysis and interpretation phase [15]. The analyst should have some training (university or short course) in mineralogy or crystallography in order to have a background in crystal structure, diffraction patterns and mineral transformation. In addition, an intensive short course in the fundamentals of X-ray diffraction can be useful.

MEASUREMENT:

11. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 $^{\circ}2\theta$) of the area air sample (or bulk settled dust) to determine the presence of free silica polymorphs and interferences (see APPENDIX). The diffraction peaks are:

| Mineral | Peak (2-Theta Degrees) | | |
|--------------|------------------------|-----------|----------|
| | Primary | Secondary | Tertiary |
| Quartz | 26.66 | 20.85 | 50.16 |
| Cristobalite | 21.93 | 36.11 | 31.46 |
| Tridymite | 21.62 | 20.50 | 23.28 |
| Silver | 38.12 | 44.28 | 77.47 |

NOTE: There is an alternative to scanning an area air sample, settled dust sample, or ground bulk sample to prove lack of contamination. A slow scan of the three main peaks of quartz (also cristobalite and tridymite if their absence has not been previously confirmed) on a personal air sample, with verification that their intensity ratios are within 15% of pure quartz, is sufficient evidence that other materials are not interfering in the silica determination.

12. Perform the following for each sample, working standard, and blank filter:
 - a. Mount the reference specimen. Determine the net intensity, I_r , of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly ($S_r < 0.01$) measured.
 - b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min (longer scan times will lower the limit of detection).
 - c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
 - d. Calculate the net intensity, I_x , (the difference between the peak integrated count and the total background count).
 - e. Calculate and record the normalized intensity, \hat{I}_x , for each peak:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N$$

NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.

- f. Determine the normalized count, \hat{I}_{Ag} , of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.
- g. Field blanks may be analyzed by scanning the 2-theta range used for the analyte and silver peaks to verify that contamination of the filters has not occurred. The analyte peak should be absent. The normalized intensity of the silver peak should match that of the media blank. Each laboratory should determine the specifics of field blank use for its application. When contamination does occur, the reason should be investigated and appropriate action taken. In practice, contamination of field blanks is extremely rare and usually is not consistent across filters. The analysis of blanks may be abbreviated if experience indicates that contamination is not likely with current field and laboratory operations; however, occasional confirmation of non-contamination is prudent.

CALCULATIONS:

13. Calculate the concentration of crystalline silica, C (mg/m^3), in the air volume sampled, V (L):

$$C = \frac{\hat{I}_x \cdot f(t) - b}{m \cdot V}, \text{mg} / \text{m}^3$$

- \hat{I}_x = normalized intensity for sample peak
 b = intercept of calibration graph (\hat{I}_x^0 vs. μg)
 m = slope of calibration graph, counts/ μg
 f(t) = $-\text{R} \ln T / (1 - T^{\text{R}})$ = absorption correction factor (Table 1)
 R = $\sin(\Theta_{\text{Ag}}) / \sin(\Theta_x)$
 T = $\hat{I}_{\text{Ag}} / (\text{average } \hat{I}_{\text{Ag}}^0)$ = transmittance of sample
 \hat{I}_{Ag} = normalized silver peak intensity from sample
 \hat{I}_{Ag}^0 = normalized silver peak intensity from media blanks (average of six values)

EVALUATION OF METHOD:

This method is based on P&CAM 259 which was collaboratively tested [1]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher (but not the use of THF), shipment of samples, ashing time, and ultrasonication time. None of these factors was found to have an effect. The method was shown to have no bias when referenced to the Talvite spectrophotometric method [14] and when all standards and samples were Min-U-Sil 5. The relative standard deviations (S_r) for intralaboratory, total measurement and overall (including sampling) variability are:

| | Analyte Level (μg) | Measurement Precision (S_r) | Overall Precision (S_{rT}) |
|------------------------------------|------------------------------------|------------------------------------|-----------------------------------|
| Intralaboratory | 50-200 | 0.08 [1] | |
| | 20 | 0.20 [5] | |
| | 10 | 0.28 [9] | |
| Total (intra- and interlaboratory) | 50-200 | 0.17 [1] | 0.29 [1] |

REFERENCES:

- [1] Anderson CC [9183]. Collaborative tests of two methods for determining free silica in airborne dust. U.S. Department of Health and Human Services, Publ. (NIOSH) 83-124.
- [2] NIOSH [1983]. User check, UBTL, NIOSH Sequence #4121-M (unpublished)
- [3] NIOSH [1974]. Criteria for a Recommended Standard: Occupational Exposure to Crystalline Silica. U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 75-120.
- [4] NIOSH [1979]. Silica, crystalline: Method P&CAM 259. In: Taylor DG, ed., NIOSH Manual of Analytical Methods, 2nd ed., Vol. 5. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 79-141.
- [5] Ibid, Vol. 3, S315. U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-C (1977).
- [6] NIOSH [1977]. Documentation of the NIOSH Validation Tests. S315, U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-185.
- [7] NIOSH [1977]. Silica (XRD): Method P&CAM 109. In: Taylor DG, ed., NIOSH Manual of Analytical Methods, 2nd ed., Vol. 1. Cincinnati, OH: U.S. Department of Health, Education, and Welfare, Publ. (NIOSH) 77-157-A.
- [8] Bumsted HE [1973]. Determination of alpha-quartz in the respirable portion of airborne particles by X-ray diffraction. *Am Ind Hyg Assoc J* 34:150.
- [9] Peters ET [1976]. Evaluation of the NIOSH X-ray diffraction method for the determination of free silica in respirable dust. Final Report, NIOSH Contract CDC-99-74-51.
- [10] Eller PM, Feng HA, Song RS, Key-Schwartz RJ, Esche CA, Groff JH [1999]. Proficiency analytical testing (PAT) silica variability, 1990-1998. *Am Ind Hyg Assoc J* 60(4):533-539.
- [11] Key-Schwartz RJ, Baron PA, Bartley DL, Rice FL, Schlecht PC [2003]. Chapter R, Determination of airborne crystalline silica. In: NIOSH Manual of Analytical Methods, 4th ed., 3rd Suppl. Cincinnati, OH: U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, DHHS (NIOSH) Publication No. 2003-154.
- [12] Inhaled Particles and Vapours [1961]. Pergamon Press, Oxford, U.K.
- [13] Kupel RE, Kinser RE, Mauer PA [1968]. Separation and analysis of the less than 10-micron fractions of industrial dusts. *Am Ind Hyg Assoc J* 29:364.

- [14] Talvitie NA [1951]. Determination of quartz in presence of silicates using phosphoric acid. *Anal Chem* 23 (4).
- [15] Hurst VJ, Schroeder PA and Styron RW [1997]. Accurate quantification of quartz and other phases by powder X-ray diffractometry. *Anal Chem Acta* 337:233-252.
- [16] Williams DD [1959]. Direct quantitative diffractometric analysis. *Anal Chem* 31:1841.
- [17] Abell MT, Dollberg DD, Crable JV [1981]. Quantitative analysis of dust samples from occupational environments using computer automated X-ray diffraction. *Advances in X-Ray Analysis* 24:37.
- [18] Abell MT, Dollberg DD, Lange BA, Hornung RW, Haartz JC [1981]. Absorption corrections in X-ray diffraction dust analyses: procedures employing silver filters. *Electron Microscopy and X-Ray Applications*, V. 2, p. 115, Ann Arbor Science Publishers, Inc.
- [19] Dollberg DD, Abell MT, Lange BA [1980]. Occupational health analytical chemistry: quantitation using x-ray powder diffraction. *ACS Symposium Series*, No. 120, 43.
- [20] Aintree-Williams S, Lee J, Mezin NV. Qualitative X-ray diffractometry on respirable dust collected on nuclepore filters. *Ann Occup Health Hyg* 20:109.
- [21] Leroux J, Powers C [1970]. Direct X-ray diffraction quantitative analysis of quartz in industrial dust films deposited on silver membrane filters. *Occup Health Rev* 21:26.

METHOD REVISED BY:

Rosa Key-Schwartz, Ph.D., Dawn Ramsey, M.S., and Paul Schlecht, NIOSH/DART.

APPENDIX: INTERFERENCES

Interferences include barite, micas (muscovite, biotite), potash, feldspars (microcline, plagioclase), montmorillonite, sillimanite, zircon, graphite, iron carbide, clinoferrosillite, wollastonite, sanidine, leucite, orthoclase, and lead sulfide.

The patterns for three forms of aluminum phosphate [JCPDS 10-423, 11-500, 20-44] are practically identical to those of quartz, cristobalite and tridymite, respectively. The quartz secondary and cristobalite primary peaks are close; cristobalite secondary peak is overlapped by a quartz peak; tridymite, if present in sufficient quantity, will interfere with all of the main (primary, secondary and tertiary) quartz and cristobalite peaks. Silver chloride, if present on the silver filter, interferes slightly with the primary quartz peak. Many of these interferences occur in the presence of quartz; however, in a study of samples collected in 11 different industries, Aintree-Williams [20] found no significant interferences.

The presence of elements such as iron can result in appreciable X-ray fluorescence which leads to high background intensity. A diffracted-beam monochromator will minimize this problem.

If calcite is present, loss of quartz will occur when samples are ashed in a muffle furnace. See SAMPLE PREPARATION (step 5.b) for procedure to remove calcite.

If interferences with the primary silica peak are present, use a less sensitive peak. When overlaps are not severe, a smaller receiving slit or chromium radiation may be used; however, a new calibration curve will be necessary.

Table 1. Absorption correction factor as a function of transmittance for some silica-silver peak combinations [16-21].

| Transmittance T | Silica Silver | f(T) (at indicated degrees 2- θ) | | | | | | | |
|--------------------|------------------|--|--------|--------|--------|--------|--------|--------|--------|
| | | 26.66 | 26.66 | 20.83 | 20.83 | 21.93 | 21.93 | 21.62 | 21.62 |
| 1.00 | | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 0.99 | | 1.0071 | 1.0082 | 1.0091 | 1.0105 | 1.0087 | 1.0100 | 1.0088 | 1.0101 |
| 0.98 | | 1.0144 | 1.0166 | 1.0184 | 1.0212 | 1.0174 | 1.0201 | 1.0177 | 1.0204 |
| 0.97 | | 1.0217 | 1.0251 | 1.0278 | 1.0321 | 1.0264 | 1.0305 | 1.0268 | 1.0309 |
| 0.96 | | 1.0292 | 1.0337 | 1.0373 | 1.0432 | 1.0355 | 1.0410 | 1.0360 | 1.0416 |
| 0.95 | | 1.0368 | 1.0425 | 1.0470 | 1.0544 | 1.0447 | 1.0517 | 1.0453 | 1.0524 |
| 0.94 | | 1.0445 | 1.0514 | 1.0569 | 1.0659 | 1.0541 | 1.0625 | 1.0548 | 1.0635 |
| 0.93 | | 1.0523 | 1.0605 | 1.0670 | 1.0776 | 1.0636 | 1.0736 | 1.0645 | 1.0747 |
| 0.92 | | 1.0602 | 1.0697 | 1.0772 | 1.0894 | 1.0733 | 1.0849 | 1.0743 | 1.0861 |
| 0.91 | | 1.0683 | 1.0791 | 1.0876 | 1.1015 | 1.0831 | 1.0963 | 1.0844 | 1.0977 |
| 0.90 | | 1.0765 | 1.0886 | 1.0982 | 1.1138 | 1.0932 | 1.1080 | 1.0945 | 1.1096 |
| 0.89 | | 1.0848 | 1.0983 | 1.1089 | 1.1264 | 1.1034 | 1.1199 | 1.1049 | 1.1216 |
| 0.88 | | 1.0933 | 1.1081 | 1.1199 | 1.1392 | 1.1137 | 1.1320 | 1.1154 | 1.1339 |
| 0.87 | | 1.1019 | 1.1181 | 1.1311 | 1.1522 | 1.1243 | 1.1443 | 1.1261 | 1.1464 |
| 0.86 | | 1.1106 | 1.1283 | 1.1424 | 1.1654 | 1.1350 | 1.1568 | 1.1370 | 1.1592 |
| 0.85 | | 1.1195 | 1.1387 | 1.1540 | 1.1790 | 1.1460 | 1.1696 | 1.1481 | 1.1722 |
| 0.84 | | 1.1286 | 1.1493 | 1.1657 | 1.1927 | 1.1571 | 1.1827 | 1.1595 | 1.1854 |
| 0.83 | | 1.1378 | 1.1600 | 1.1777 | 1.2068 | 1.1685 | 1.1959 | 1.1710 | 1.1989 |
| 0.82 | | 1.1471 | 1.1709 | 1.1899 | 1.2211 | 1.1800 | 1.2095 | 1.1827 | 1.2126 |
| 0.81 | | 1.1566 | 1.1821 | 1.2024 | 1.2357 | 1.1918 | 1.2232 | 1.1946 | 1.2266 |
| 0.80 | | 1.1663 | 1.1934 | 1.2150 | 1.2506 | 1.2038 | 1.2373 | 1.2068 | 1.2409 |
| 0.79 | | 1.1762 | 1.2050 | 1.2280 | 1.2658 | 1.2160 | 1.2516 | 1.2192 | 1.2555 |
| 0.78 | | 1.1863 | 1.2168 | 1.2411 | 1.2812 | 1.2284 | 1.2663 | 1.2319 | 1.2703 |
| 0.77 | | 1.1965 | 1.2288 | 1.2546 | 1.2971 | 1.2411 | 1.2812 | 1.2447 | 1.2855 |
| 0.76 | | 1.2069 | 1.2410 | 1.2683 | 1.3132 | 1.2540 | 1.2964 | 1.2579 | 1.3009 |
| 0.75 | | 1.2175 | 1.2535 | 1.2822 | 1.3297 | 1.2672 | 1.3119 | 1.2713 | 1.3167 |
| 0.74 | | 1.2283 | 1.2662 | 1.2965 | 1.3456 | 1.2806 | 1.3278 | 1.2849 | 1.3328 |
| 0.73 | | 1.2394 | 1.2792 | 1.3110 | 1.3637 | 1.2944 | 1.3440 | 1.2989 | 1.3493 |
| 0.72 | | 1.2506 | 1.2924 | 1.3259 | 1.3812 | 1.3084 | 1.3605 | 1.3131 | 1.3661 |
| 0.71 | | 1.2621 | 1.3059 | 1.3410 | 1.3991 | 1.3226 | 1.3774 | 1.3276 | 1.3883 |
| 0.70 | | 1.2738 | 1.3197 | 1.3565 | 1.4174 | 1.3372 | 1.3946 | 1.3424 | 1.4008 |
| 0.69 | | 1.2857 | 1.3337 | 1.3723 | 1.4362 | 1.3521 | 1.4122 | 1.3576 | 1.4187 |
| 0.68 | | 1.2979 | 1.3481 | 1.3885 | 1.4553 | 1.3673 | 1.4303 | 1.3730 | 1.4370 |
| 0.67 | | 1.3103 | 1.3682 | 1.4050 | 1.4749 | 1.3829 | 1.4487 | 1.3888 | 1.4558 |
| 0.66 | | 1.3230 | 1.3777 | 1.4218 | 1.4949 | 1.3987 | 1.4675 | 1.4050 | 1.4749 |
| 0.65 | | 1.3359 | 1.3931 | 1.4390 | 1.5154 | 1.4150 | 1.4868 | 1.4215 | 1.4945 |
| 0.64 | | 1.3491 | 1.4087 | 1.4567 | 1.5363 | 1.4316 | 1.5064 | 1.4383 | 1.5145 |
| 0.63 | | 1.3626 | 1.4247 | 1.4747 | 1.5578 | 1.4485 | 1.5266 | 1.4556 | 1.5350 |
| 0.62 | | 1.3765 | 1.4411 | 1.4931 | 1.5797 | 1.4659 | 1.5472 | 1.4732 | 1.5560 |
| 0.61 | | 1.3906 | 1.4578 | 1.5120 | 1.6022 | 1.4836 | 1.5684 | 1.4913 | 1.5775 |
| 0.60 | | 1.4050 | 1.4749 | 1.5314 | 1.6252 | 1.5018 | 1.5900 | 1.5098 | 1.5995 |
| 0.59 | | 1.4198 | 1.4925 | 1.5511 | 1.6488 | 1.5204 | 1.6122 | 1.5287 | 1.6221 |
| 0.58 | | 1.4349 | 1.5104 | 1.5714 | 1.6730 | 1.5394 | 1.6349 | 1.5481 | 1.6452 |
| 0.57 | | 1.4504 | 1.5288 | 1.5922 | 1.6978 | 1.5590 | 1.6582 | 1.5679 | 1.6689 |
| 0.56 | | 1.4662 | 1.5476 | 1.6135 | 1.7233 | 1.5790 | 1.6820 | 1.5883 | 1.6932 |
| 0.55 | | 1.4824 | 1.5670 | 1.6353 | 1.7494 | 1.5995 | 1.7065 | 1.6092 | 1.7181 |
| 0.54 | | 1.4991 | 1.6858 | 1.6577 | 1.7762 | 1.6205 | 1.7317 | 1.6306 | 1.7437 |
| 0.53 | | 1.5161 | 1.6071 | 1.6807 | 1.8037 | 1.6421 | 1.7575 | 1.6525 | 1.7699 |
| 0.52 | | 1.5336 | 1.6279 | 1.7043 | 1.8319 | 1.6642 | 1.7840 | 1.6751 | 1.7969 |
| 0.51 | | 1.5515 | 1.6493 | 1.7285 | 1.8609 | 1.6870 | 1.8112 | 1.6982 | 1.8246 |
| 0.50 | | 1.5699 | 1.6713 | 1.7534 | 1.8908 | 1.7103 | 1.8391 | 1.7220 | 1.8531 |