

Department of Labor
Mine Safety and Health Administration
Technical Support
Pittsburgh Safety and Health Technology Center

MSHA P-2: X-RAY DIFFRACTION DETERMINATION OF QUARTZ AND
CRISTOBALITE IN RESPIRABLE METAL/NONMETAL MINE DUST

Matrix/Media: Respirable Metal/Nonmetal Mine Dust/Filters

Range: 10-300 µg Quartz and Cristobalite

Reporting Limit: 10 µg Quartz and 20 µg Cristobalite

Detection Limit: 2 µg Quartz and 10 µg Cristobalite

Precision: 13% Sampling and Analytical Error, 11% Analytical Error

PRINCIPLE OF METHOD

Airborne respirable dust samples are collected on preweighed polyvinyl chloride (PVC) filters using approved personal respirable dust samplers. After sample collection, the filter capsules are reweighed to one thousandth of a milligram (mg) to determine the net sample mass. The sample filters are ashed in a low-temperature radio-frequency (RF) generated oxygen-plasma asher to remove the organic matrix and media. Ashed samples are deposited onto an approximately 13-millimeter (mm) diameter area of a silver membrane filter. The redeposited, ashed dust samples are scanned by X-ray Diffraction (XRD) at four defined angles to determine the quartz content and/or at three angles to determine the cristobalite content. Tridymite can also be determined qualitatively by request, although it is not commonly found.

1. Responsibilities

- 1.1. All analysts performing this procedure must have the necessary training completed and signed by the supervisor.
- 1.2. It is the responsibility of the analyst to follow this procedure as written. Any deviations of the procedure must be approved by the supervisor and documented. Supplemental work instructions must also be followed as written.
- 1.3. The Turn-Around Time (TAT) goal for metal/nonmetal (MNM) silica samples is 8 days from laboratory receipt.
- 1.4. A back-up analyst shall be trained and competent in this procedure.
- 1.5. The analyst is responsible for reviewing data and calculations for accuracy and completeness before giving the results to the authorized personnel for validation and approval.

- 1.6. Calculations are performed using the calculation spreadsheet. This spreadsheet shall be checked annually for accuracy by the analyst or other approved personnel.

2. SAFETY

- 2.1. Laboratory coats, gloves, and safety glasses shall be worn when working with acids. Gloves and safety glasses should be worn when working with isopropanol (IPA). Ear plugs may also be worn during sample sonication.
- 2.2. Each chemical should be regarded as a potential health hazard, and the exposure to these compounds should be as low as reasonably achievable. Every individual performing this procedure should be familiar with the Safety Data Sheets (SDS) for every material used.
- 2.3. IPA is flammable and should be used in a fume hood or a well-ventilated area and stored in a flammable cabinet.
- 2.4. Concentrated acids are toxic and extremely irritating to skin and mucous membranes. Acids must be handled in a fume hood.
- 2.5. Respirable Crystalline Silica (RCS) is a carcinogen. Laboratory controls should be in place to minimize exposure to RCS.
- 2.6. Radiation badges shall be worn by analysts to detect exposure to low-level radiation. Radiation badges are also placed on each instrument. Badges are collected quarterly to determine exposure.

3. MATERIALS

- 3.1. Isopropanol (IPA)
- 3.2. NIST Quartz Standard Reference Material (SRM), Respirable Alpha Quartz
- 3.3. NIST Cristobalite SRM, Respirable Cristobalite
- 3.4. Reference sample (corundum or other stable standard) used for data normalization. Also known as the 'monitor' sample
- 3.5. Collodion/Parlodion, 2% in Amyl Acetate. Used for adhering standards onto the silver membrane filter. Either commercially prepared or prepared by adding 2 grams of a parlodion strip to a flask and diluting to 100 mL with amyl acetate
- 3.6. Deionized water
- 3.7. Acid Washing: Nitric Acid (concentrated), Phosphoric Acid (85%, reagent grade), Fluoroboric Acid (48-50%, reagent grade), and Ammonium Hydroxide (30% aqueous ammonia)

4. EQUIPMENT AND SUPPLIES

4.1. Volumetric Measurement and Glassware

- 4.1.1. Beakers, Pyrex, 50 mL
- 4.1.2. Volumetric pipettes, Class A
- 4.1.3. Mechanical autopipette, meeting required certification standards
- 4.1.4. Volumetric flasks, Class A

4.2. X-ray Diffractometer

- 4.2.1. Malvern PANalytical CubiX³, Bruker D4 Endeavor or equivalent with copper target x-ray tube optimized for maximum intensity
- 4.2.2. XRD sample holders for 25 mm filters

4.3. Weighing

- 4.3.1. Microbalance, capable of weighing to 0.001 milligrams; Mettler XP6 or equivalent
- 4.3.2. Spatula, stainless steel
- 4.3.3. Weighing boats

4.4. Filters

- 4.4.1. Polyvinylchloride (PVC) Filters, 37 mm diameter, 5.0 μm pore size
- 4.4.2. Silver Membrane Filters, 25 mm diameter, 0.45 μm pore size

4.5. Filtration

- 4.5.1. Filtration apparatus consisting of a manifold, fritted support bases, clamps, rubber stoppers, vacuum tubing, and a side-arm filtering flask
- 4.5.2. Aluminum filtering funnels, specially fabricated with an approximately 13 mm diameter bore area. Note: All funnels used for calibration and analysis must have the same bore diameter
- 4.5.3. Aluminum rings, specially fabricated to fit the aluminum funnels and fritted support bases. These are used to center the deposit on the filter
- 4.5.4. Vacuum pump.
- 4.5.5. Glass filtration funnel and fritted glass base (used for acid washing)

4.6. Miscellaneous Equipment

- 4.6.1. Low-temperature RF generated oxygen plasma asher and vacuum pump, Anatech Model SCE-604 or equivalent
- 4.6.2. Oxygen cylinder with a two-stage regulator capable of being set at 0 to 60 psi

- 4.6.3. Nitrogen cylinder with a two-stage regulator capable of being set at 0 to 200 psi
- 4.6.4. Stainless steel forceps used to handle filters and open cassettes
- 4.6.5. Petri slides capable of holding 47 mm diameter filters; Millipore PDMA04700 or equivalent
- 4.6.6. Ultrasonic bath, 200-watt input
- 4.6.7. Wash bottles, polyethylene
- 4.6.8. Desiccator
- 4.6.9. Slide warmer
- 4.6.10. Pipette bulb, rubber or neoprene
- 4.6.11. Nitrile gloves
- 4.6.12. Drying oven
- 4.6.13. 10 μ m-sieve
- 4.6.14. Mortar and pestle

5. INTERFERENCES

- 5.1. Interferences due to mineral dusts other than crystalline silica may be encountered. If an interference occurs and needs to be resolved, the first approach is to use alternate diffraction angles and utilize computer assisted methods of integration. If the interference is still present, chemical treatment or acid washing should be performed on the sample.

6. CALIBRATION

- 6.1. Calibration standards are prepared on silver membrane filters from a suspension of NIST SRM in IPA. The most recently approved version of the calibration work instructions should be followed. These standards will be prepared in triplicate and will consist of six different concentrations falling within and completely covering the concentration range.
- 6.2. Calibrations are validated by a set of Independent Calibration Verification (ICV) standards. These standards are prepared from a separately prepared suspension by a separate analyst following the most recent approved version of the calibration work instructions. These standards typically consist of three different concentrations prepared in duplicate that fall within the concentration range.
- 6.3. All standards used in the calibration and validation of the calibration are corrected for the crystallinity of the NIST certified value and are prepared on silver membrane filters using the same filtration apparatus used for preparing the enforcement samples.
- 6.4. Calibrations are approved by the supervisor or other designated personnel when all criteria in the calibration spreadsheet is met or reviewed and justified by the approver.

- 6.5. Once the calibration is approved, a calibration factor is determined for each diffraction angle by using the average response factor (peak area/ μg) or a linear regression for all standards after removing any outliers.
- 6.6. Instruments are calibrated at least once annually. However, the calibration may be done more often if necessary. Instrument maintenance or a corrective action after a non-conforming event may prompt recalibration of an instrument.
- 6.7. After instrument maintenance, a calibration check shall be performed and documented before placing the instrument back into service.

7. SAMPLE PREPARATION

- 7.1. The most recently approved version of the XRD work instructions should be followed for all sample preparation.

Filters

- 7.2. MNM enforcement filters meeting the silica analysis requirements are analyzed by XRD. Samples not meeting the silica analysis requirements are not analyzed and are documented as "Analysis Not Performed" or "ANP". If any sample mass exceeds the limit for deposit loading, the sample is split into increments or subsamples, processed and then analyzed. The subsample results are combined for a total single result.
- 7.3. Prepare and process filter samples as batches. Batches can include up to 19 enforcement samples. In addition to those samples the batch must include one field blank, one method blank, and three quality assurance known samples. All samples are carried through the entire process.
- 7.4. Open filter capsules with forceps. Remove the filter and place it dust-side down in the bottom of a beaker. Place each sample into separate beakers. Any filter abnormalities should be recorded.
- 7.5. Place the entire batch of sample in a low temperature asher and run for about 90 minutes until all samples have been ashed completely.
- 7.6. After ashing, carefully remove each beaker from the asher and add approximately 10 mL of IPA along the edge of the beaker using a squeeze bottle. Be sure there is no ash lost while adding IPA to each beaker.
- 7.7. Place up to six beakers in an ultrasonic bath and sonicate for several minutes to disperse the ash in the IPA.
- 7.8. Prepare the filtration apparatus for depositing the samples. Using forceps, place a silver membrane filter onto the fritted glass base inside the aluminum ring and position the funnel securely over the silver membrane filter using the clamp. Check for leaks before depositing the sample on the filter by adding IPA to each funnel and turning on the vacuum and opening the stopcock. Correct any leaks by repositioning the funnel or clamp before depositing the sample.

- 7.9. Carefully deposit the sample onto the silver membrane filter by pouring the suspension into the funnel. Rinse the inverted beaker with IPA from a squeeze bottle so that the rinse solution will drain directly into the funnel.
- 7.10. When the depth of the liquid in the funnel reaches about 2 cm above the filter, apply a final rinse of IPA to the funnel walls using the squeeze bottle. Be sure to not disturb the deposit during the final rinse.
- 7.11. After all the IPA has drained from the silver membrane filter, maintain suction to partially dry the sample.
- 7.12. Keeping the vacuum on, remove the funnel. Then turn off the vacuum and remove the silver membrane filter from the fritted base using forceps. Only touch the edge of the filter and not the deposit.
- 7.13. Mark the edge of the filter with sample identification and place on the slide warmer to dry completely.
- 7.14. Repeat steps 7.7 through 7.13 until all samples in the batch are processed.

Bulks

- 7.15. Depending on the state of the bulk upon receipt, a mortar and pestle may be needed to crush the material into smaller pieces.
- 7.16. Wet sieve a portion of the bulk material into a beaker or glass dish with a 10 μm -sieve, IPA and an ultrasonic bath until there is enough sieved material for a subsample of approximately 1 mg.
- 7.17. Allow the excess alcohol to evaporate by drying in an oven at 100°C or placing the beaker of material on a slide warmer for approximately two hours. Store in a desiccator until the sample is cool.
- 7.18. Using a microbalance, weigh 0.5-1.0 mg of dust onto a PVC filter. Then place the PVC filter dust-side down in a beaker.
- 7.19. Ash the sample in a low temperature asher for approximately 90 minutes with a batch of enforcement filters as well as a FB, MB, and three quality assurance known samples.
- 7.20. Follow steps 7.6 through 7.14 to prepare the sample for analysis.

8. QUALITY ASSURANCE SAMPLES

- 8.1. The *Monitor* is an instrument check used to normalize the data due to tube drift. A NIST certified reference material made of corundum is used.
- 8.2. The *Reporting Limit (RL)* is a low-level calibration standard made from the same stock as the calibration standards. The RL is used to check the instrument performance and is analyzed at least once per batch.
- 8.3. The *Continuing Calibration Verification (CCV)* is a mid-level calibration standard made from the same stock as the calibration standards. The CCV is used to check the instrument performance and is analyzed at least once per batch.

- 8.4. The *Independent Calibration Verification (ICV)* is typically comprised of multiple concentration levels within the calibration range and is made from a stock independent of the calibration standards, RL, and CCV. The ICV standards are analyzed at least once annually to verify the calibration.
- 8.5. The *Method Blank (MB)* is a clean PVC filter placed into a beaker and treated in the same manner as a sample. The MB is used to determine if contamination exists in the filter or occurred during the sample preparation process.
- 8.6. The *Field Blank (FB)* is an unused filter capsule carried in the field during sampling and is submitted with enforcement samples. At least one FB shall be prepared and analyzed with each batch of samples.
- 8.7. The *Knowns* are samples of a known quartz and/or cristobalite mass that go through the entire sample preparation process. Typically, the knowns contain between 0.075-0.125 mg of the target analyte but must at least have a known analyte mass that falls within the calibration range. Knowns are prepared by weighing out certified material onto a clean PVC filter. They are analyzed in triplicate with each batch and are carried through the entire sample preparation process. Knowns are used to determine precision and validate the sample preparation per each batch.

9. XRD ANALYSIS

- 9.1. Mount the batch of prepared silver filter samples in the XRD sample holders. Be sure the deposit is centered in the holder and the silver membrane filter lays flat.
- 9.2. Follow and record all function verification procedures before running any samples on the instrument. Once all checks are completed and acceptable, analysis of the samples may begin.
- 9.3. Analyze the batch of samples and the appropriate quality assurance samples by the XRD instrument at the primary angle (quartz and/or cristobalite) and a silver angle. The most recently approved work instructions should be followed.
- 9.4. A monitor sample is analyzed at set intervals to determine and correct for instrument drift due to tube degradation, power fluctuations, and environmental conditions. The result of the monitor is used to adjust the peak areas and normalize the sample results.
- 9.5. Once all samples have been analyzed by the XRD, use the instrument software to view and fit each sample. Peak areas are determined and the analyte mass for each sample is calculated using the calibration factor. Follow the most recently approved work instructions to fit each sample.
- 9.6. Samples exceeding the permissible exposure limit (PEL) for quartz and/or cristobalite calculated from the primary angle are analyzed at additional angles. For the quartz analysis there are a total of three additional angles that can be used to verify the results of the primary angle. For the cristobalite analysis there are two additional angles that can be used to verify the results of the primary angle.

10. DATA REVIEW

- 10.1. The analyst reviews all the data using the calculation spreadsheet and then signs off on the results. If any failures occurred in the batch, a non-conforming event must be reported.
- 10.2. The supervisor or other designated personnel reviews the sample results, calculations, QA data, and any applicable non-conforming events. If acceptable, the batch is validated and approved.
- 10.3. For samples with a silica mass less than the detection limit, the result is documented as less than the detection limit for the desired analyte.
- 10.4. For samples with a silica mass greater than the highest calibration standard, the sample result is confirmed by additional angles and is then documented as greater than the highest calibration standard.
- 10.5. When finalized, the sample results are transferred to the MSHA databases along with the reporting limit value for all analytes.

11. CALCULATIONS

Table 1: Variables and Formulas used in Calculations

Variable	Formula	Description	Example Values
m	=	Calibration factor (average response factor, peak area/ μg)	136
I_x	=	Silica peak area for sample	5720
d	=	Corundum peak area (reference specimen)	3287
d_0	=	Corundum peak area (reference specimen at calibration)	4250
N	= d_0/d	Normalization factor	1.29
I_{Ag}	=	Silver peak area for sample filter	5238
I^0_{Ag}	=	Average of silver peak areas for knowns, MB, FB in sample run	5936
\hat{I}_x	= $I_x \times N$	normalized silica peak area for sample	7379
\hat{I}_{Ag}	= $I_{Ag} \times N$	Normalized silver peak area for sample filter	6757
\hat{I}^0_{Ag}	= $I^0_{Ag} \times N$	Normalized average of silver peak areas for knowns, MB, FB in sample run	7657
T	= $\hat{I}_{Ag} / \hat{I}^0_{Ag}$	transmittance of sample	0.882
θ_{Ag}	= $2\theta_{Ag}/2$	angle of silver (example for 44.28° 2θ silver peak)	22.14
θ_x	= $2\theta_x/2$	angle of silica (example for the 26.66° 2θ quartz peak)	13.33
R	= $\sin(\theta_{Ag})/\sin(\theta_x)$	(example for 44.28° 2θ silver peak and the 26.66° 2θ quartz peak)	1.6346
f(t)	= $-R \times \ln T / (1 - T^R)$	absorption correction factor	1.106

11.1. Quartz mass calculation using the formulas and example values found in Table 1.

Absorption Correction Factor

$$f(T) = -R \times \frac{\ln T}{(1 - T^R)}$$

$$2\theta_{Ag} = 44.28^\circ \quad 2\theta_X = 26.66^\circ$$

$$\theta_{Ag} = \frac{2\theta_{Ag}}{2} \quad \theta_X = \frac{2\theta_X}{2}$$

$$R = \frac{\sin \theta_{Ag}}{\sin \theta_X}$$

$$R = \frac{\sin 22.14^\circ}{\sin 13.33^\circ}$$

$$R = 1.6346$$

$$T = \frac{\hat{I}_{Ag}}{\hat{I}_{Ag}^0}$$

$$T = \frac{6757}{7657}$$

$$T = 0.882$$

$$f(T) = -R \times \frac{\ln T}{(1 - T^R)}$$

$$f(T) = -1.6346 \times \frac{\ln 0.882}{(1 - 0.882^{1.6346})}$$

$$f(T) = 1.106$$

Quartz Mass (μg)

$$\text{Quartz Mass} = \hat{I}_X \times \frac{f(t)}{m}$$

$$\hat{I}_X = I_X \times N$$

$$N = \frac{d_0}{d}$$

$$N = \frac{4250}{3287}$$

$$N = 1.29$$

$$\hat{I}_X = 5720 \times 1.29$$

$$\hat{I}_X = 7379$$

$$\text{Quartz Mass} = \hat{I}_X \times \frac{f(t)}{m}$$

$$\text{Quartz Mass} = 7379 \times \frac{1.106}{136}$$

$$\text{Quartz Mass} = 60 \mu\text{g}$$

11.2. Air sampling volume calculation using the sample flowrate and sampling time.

$$\text{Air Volume (m}^3\text{)} = \frac{\text{Flowrate } \left(\frac{\text{L}}{\text{min}}\right) \times \text{Sampling Time (minutes)}}{1000 \left(\frac{\text{L}}{\text{m}^3}\right)}$$

11.3. Quartz concentration using the measured quartz mass, air sampling volume, and any appropriate corrections.

$$\text{Quartz Concentration} \left(\frac{\mu\text{g}}{\text{m}^3}\right) = \frac{\text{Quartz Mass } (\mu\text{g})}{\text{Air Volume (m}^3\text{)}}$$

11.4. Bulk samples are reported as an approximation and are used to estimate silica content.

$$\sim\% \text{Analyte} = \frac{\text{Analyte Mass } (\mu\text{g})}{\text{Sample Mass } (\mu\text{g})} \times 100$$

12. DISPOSAL

12.1. IPA will be disposed of as a liquid organic waste. All acids will be disposed of as a liquid inorganic waste.

12.2. The silver membrane filters and bulks are considered solid inorganic hazardous waste and must be disposed of accordingly.

13. REFERENCES

13.1. OSHA ID-142, Crystalline Silica Quartz and Cristobalite, Sampling and Analytical Methods, Fourth Edition, May 2016.

13.2. NIOSH 7500, Silica, crystalline, by XRD, NIOSH Manual of Analytical Methods, Fourth Edition, 3/15/2003.

13.3. All P-2 work instructions are internal laboratory documents.