

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

**MSHA P-7: INFRARED SPECTROSCOPY DETERMINATION OF QUARTZ IN  
RESPIRABLE COAL MINE DUST**

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Matrix/Media: Respirable Coal Mine Dust/Filters

Range: 10-300  $\mu\text{g}$  Quartz

Reporting Limit: 10  $\mu\text{g}$  Quartz

Detection Limit: 3  $\mu\text{g}$  Quartz

Precision: 8.8% Sampling and Analytical Error, 5.3% Analytical Error

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## **PRINCIPLE OF METHOD**

Airborne respirable dust samples are collected on preweighed membrane 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 9-millimeter (mm) diameter area of a polyethylene (PE) filter. The redeposited, ashed dust samples are scanned using a Fourier Transform Infrared Spectrometer (FTIR) between 1,000 and 600 wavenumbers ( $\text{cm}^{-1}$ ) to determine the quartz and kaolinite content. The mass of quartz in the deposit is quantified by comparison to calibration curves for standard quartz samples and standard kaolinite samples.

### **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 analyst to follow this procedure as written. Any deviations of this 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 coal silica samples is 6 days from the 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 MSHA FTIR Analysis program and calibration spreadsheet. This program and spreadsheet shall be checked annually for accuracy by the analyst or other approved personnel.

## 2. SAFETY

- 2.1. Laboratory coats, gloves, and safety glasses should be worn when performing this procedure. Ear plugs may also be used 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 Sheet (SDS) for every material used.
- 2.3. Isopropanol (IPA) is flammable and should be used in a fume hood or well-ventilated area and stored in a flammable cabinet.
- 2.4. Respirable Crystalline Silica (RCS) is a carcinogen. Laboratory controls should be in place to minimize exposure to RCS.

## 3. MATERIALS

- 3.1. Isopropanol (IPA)
- 3.2. NIST Quartz Standard Reference Material (SRM), Respirable Alpha Quartz
- 3.3. Kaolinite; Imerys Kaolin, Hydrite UF or equivalent
- 3.4. Minusil; US Silica or equivalent

## 4. EQUIPMENT AND SUPPLIES

- 4.1. Volumetric Measurement and Glassware
  - 4.1.1. Volumetric pipettes, Class A
  - 4.1.2. Mechanical autopipette, meeting required certification standards
  - 4.1.3. Volumetric flasks, Class A
  - 4.1.4. Beakers, Pyrex, 50 mL
- 4.2. Fourier Transform Infrared Spectrometer (FTIR)
  - 4.2.1. Sample holders for FTIR – custom made steel plates with a center hole having a diameter the same size as, or slightly smaller than, that of the approximately 9 mm sample deposit
  - 4.2.2. Small ring magnets used to hold the filters in position on the sample holder

#### 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  $\mu\text{m}$  pore size
- 4.4.2. Polyethylene (PE) Filters, 19 mm diameter, 0.45  $\mu\text{m}$  pore size
- 4.4.3. Glass Fiber Filters, 25 mm diameter
- 4.4.4. Nuclepore Polycarbonate Filters, 25 mm diameter

#### 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 9 mm bore diameter  
  
Note: All funnels used for calibration and analysis have approximately the same bore diameter.
- 4.5.3. Aluminum rings, specially fabricated to fit the aluminum funnels and fritted support bases  
  
Note: These are used to center the deposit on the filter.
- 4.5.4. Vacuum pump

#### 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-whatt 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  $\mu\text{m}$ -sieve
- 4.6.14. Mortar and pestle
- 4.6.15. Diamond marking pencil or engraving tool
- 4.6.16. Polystyrene film (0.038 mm thickness)

## 5. INTERFERENCES

- 5.1. Interferences within the analyte spectrum are mitigated through several means.
  - 5.1.1. Background sloping interferences are removed utilizing the instrument software.
  - 5.1.2. Non-quantified interferences at baseline endpoints are removed by adjustment of the baseline endpoint selection such that the proper area of quartz is selected.
  - 5.1.3. Kaolinite, a common interference at  $800\text{ cm}^{-1}$ , is accounted for in its own calibration and is then used to correct for the total peak area at  $800\text{ cm}^{-1}$ .

## 6. CALIBRATION

- 6.1. Calibrations are performed using a series of calibration standard samples prepared from suspensions in IPA of NIST SRM for quartz and Hydrite UF for kaolinite. These suspensions are used to prepare standards on PE filters. The most recently approved version of the calibration work instructions should be followed. These standard samples shall consist of six different concentrations falling within and completely covering the calibration range. These standard samples must be prepared in at least triplicate.
- 6.2. Calibrations are validated by a set of Independent Calibration Verification (ICV) standards. These standards shall be prepared by a separate analyst from a separately prepared suspension following the most recent approved calibration work instructions. The ICV standards typically consist of two or three different concentrations prepared in at least duplicate that fall within the calibration range.
- 6.3. All standards used in the calibration and validation of the calibration are deposited on PE filters using the same filtration apparatus used for preparing enforcement samples.
- 6.4. Calibrations are approved by the supervisor or other designated personnel when all criteria in the calibration spreadsheet are met or reviewed and justified by the approver.

- 6.5. Once the calibration is approved, a calibration factor is determined for quartz by averaging the response factor (area/ $\mu\text{g}$ ) for all standards after removing any outliers. Quartz is measured using the peak area at  $800\text{ cm}^{-1}$ . For kaolinite, the peak area is measured at  $800\text{ cm}^{-1}$  and  $915\text{ cm}^{-1}$ . A ratio is then calculated comparing the kaolinite area at  $915\text{ cm}^{-1}$  against the area at  $800\text{ cm}^{-1}$ . This ratio is used to correct the total peak area at  $800\text{ cm}^{-1}$  for any kaolinite contribution, so quartz mass alone is calculated for the sample.
- 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 FTIR work instructions should be followed for all sample preparation.

### Filters

- 7.2. Coal enforcement samples meeting the quartz analysis requirements are analyzed by FTIR. 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 samples as batches. Batches can include up to 25 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 samples in a low temperature asher and run for about 60 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 two glass fiber filters on each fritted support base to act as a backup pad. On top of the glass fiber filters, place the aluminum ring. One PE filter is positioned inside the aluminum

ring and the funnel is securely clamped to hold everything together. 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 one of beaker samples onto a PE filter by pouring the suspension into the funnel. Rinse the inverted beaker with IPA from a squeeze bottle so that the rinse will drain directly into the funnel.
- 7.10. When the depth of the liquid in the funnel reaches about 2 cm above the filter, gently rinse the inside of the funnel with IPA. Be sure to not disturb the deposit during the final rinse.
- 7.11. After all the IPA has drained from the PE filter, maintain suction to partially dry the filter. Keeping the vacuum on, remove the clamp and funnel while taking care to not scrape or disturb the deposit.
- 7.12. Turn the vacuum off and remove the PE filter from the fritted support base using forceps by only touching the edge of the filter, not the deposit.
- 7.13. Mark the edge of the filter with sample identification and store the filter in a petri slide. Place the petri slide on a slide warmer for approximately 15 minutes until the filter is completely dry.
- 7.14. Repeat steps 7.7 through 7.13 until all sample 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  $\mu\text{m}$ -sieve, IPA, and an ultrasonic bath until there is enough sieved material for a representative amount. Allow sieved material to sonicate for several minutes.
- 7.17. Set up the filtration apparatus with the appropriate preweighed filter. The filtering funnel may vary depending on the diameter of the filter used. Deposit diameter is not vital as this step. Be sure there are no leaks before filtering by adding IPA to the funnel and turning on the vacuum and opening the stopcock. Adjust funnel and clamp if necessary.
- 7.18. Using a pipette, deposit a portion of the sample on to the preweighed filter.
- 7.19. Remove the filter from the filtration apparatus and allow the filter to dry completely on a hot plate.
- 7.20. Once completely dry and cooled, weigh the filter with the deposit. The bulk sample mass is determined by calculating the difference between the pre and post weight of the filter. The ideal sample mass is 1 mg.

- 7.21. Batches containing a bulk should have three knowns prepared on an appropriate mass stable filter media that matches the media used in 7.17. There may not be a FB or MB for batches containing a bulk. All samples in the batch should be ashed, redeposited on a PE filter and prepared following steps 7.5 through 7.14.

## 8. QUALITY ASSURANCE SAMPLES

- 8.1. The *Method Blank (MB)* is a clean PVC filter from the lab that is placed into a beaker and is 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.
- 8.2. The *Field Blank (FB)* is an unused filter capsule carried in the field during sampling and is submitted with enforcement samples. Typically, one FB is prepared and analyzed with each batch of samples.
- 8.3. 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.
- 8.4. 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.
- 8.5. 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.
- 8.6. The *Knowns* are samples of a known quartz concentration that go through the sample preparation process. Typically, the mass of a known is 0.075-0.125 mg of quartz and is prepared by weighing out Minusil onto a clean PVC filter. Knowns are analyzed in triplicate with each batch and are carried through the entire sample preparation process. They are used to determine precision and validate the sample preparation process per each batch.

## 9. FTIR ANALYSIS

- 9.1. 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.
- 9.2. The most recently approved work instructions should be followed to analyze a batch of samples and the appropriate quality assurance samples. When placing the sample in the instrument be sure that deposit is centered in the holder before measuring the absorbance.

- 9.3. Once all samples in the batch have been analyzed, the instrument software and MSHA FTIR Analysis program shall be used to view the spectrum, correct the sloping background, and adjust background points if necessary.
- 9.4. After all sample spectra has been reviewed and corrected by the analyst, the quartz mass is calculated using the peak areas, calibration factor, and kaolinite ratio.
- 9.5. Samples with a quartz mass exceeding the highest calibration factor will be split and reanalyzed. This means they will be resuspended in IPA and the appropriate number of portions will be redeposited onto PE filters. All portions of the original sample shall have a quartz mass within the calibration range. All splits and the originally deposited PE filter (after splitting) will be analyzed, and the results combined for a total single result.
- 9.6. Samples exceeding the permissible exposure limit (PEL) or a predetermined specified mass will be rescanned to verify the original result. Any discrepancies will be reconciled before the final result is validated and approved.

## 10. DATA REVIEW

- 10.1. The analyst reviews all the data and review sheets before signing 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, QA data, spectra and any applicable non-conforming events. If acceptable, the batch is validated and approved.
- 10.3. For samples with a quartz mass less than the detection limit, the result is documented as below the detection limit.
- 10.4. When finalized, the sample results are transferred to the MSHA databases where the reporting limit is noted.

## 11. CALCULATIONS

Table 1. Example values for calculations.

Description	Example Values
Quartz calibration factor (quartz area/ $\mu\text{g}$ ) at $800\text{ cm}^{-1}$	0.065
Kaolinite ratio determined from the kaolinite calibration by taking the average peak area of kaolinite at $915\text{ cm}^{-1}$ divided by the average peak area of kaolinite at $800\text{ cm}^{-1}$	3.2
Total peak area at $800\text{ cm}^{-1}$ (uncorrected for kaolinite)	4.163
Peak area of kaolinite at $915\text{ cm}^{-1}$	0.935
Peak area of kaolinite at $800\text{ cm}^{-1}$	0.292



11.1. Kaolinite corrected quartz area calculation on the total peak area at 800 cm<sup>-1</sup>.

$$\text{Kaolinite Peak Area at } 800 \text{ cm}^{-1} = \frac{\text{Kaolinite Peak Area at } 915 \text{ cm}^{-1}}{\text{Kaolinite Ratio}_{(915/800)}}$$

$$\text{Kaolinite Peak Area at } 800 \text{ cm}^{-1} = \frac{0.935}{3.2}$$

$$\text{Kaolinite Peak Area at } 800 \text{ cm}^{-1} = 0.292$$

$$\begin{aligned} &\text{Corrected Quartz Area at } 800 \text{ cm}^{-1} \\ &= \text{Total Peak Area at } 800 \text{ cm}^{-1} - \text{Kaolinite Peak Area at } 800 \text{ cm}^{-1} \end{aligned}$$

$$\text{Corrected Quartz Area at } 800 \text{ cm}^{-1} = 4.163 - 0.292$$

$$\text{Corrected Quartz Area at } 800 \text{ cm}^{-1} = 3.871$$

11.2. Quartz mass (μg)

$$\text{Quartz Mass} = \frac{\text{Corrected Quartz Area at } 800 \text{ cm}^{-1}}{\text{Quartz Calibration Factor}}$$

$$\text{Quartz Mass} = \frac{3.871}{0.065}$$

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

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

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

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

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

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

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

## 12. DISPOSAL

- 12.1. IPA will be disposed of as a liquid organic waste.
- 12.2. All filters and bulks are considered solid inorganic hazardous waste and must be disposed of accordingly.

## 13. REFERENCES

- 13.1. NIOSH 7603, Quartz in Respirable Coal Mine Dust, by IR, NIOSH Manual of Analytical Methods, Fifth Edition, 7/25/2017.
- 13.2. Anderson, C. C. Collaborative Tests of Two Methods for Determining Free Silica in Airborne Dust DHHS (NIOSH) Publication No. 83-124; Contract No. 210-79-0059, February 1983.
- 13.3. All P-7 work instructions are internal documents.

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