

QUARTZ in coal mine dust, by IR (redeposition)

7603

SiO₂

MW: 60.08

CAS: 14808-60-7

RTECS: VV7330000

METHOD: 7603, Issue 3

EVALUATION: UNRATED

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OSHA : quartz (respirable):
10 mg/m³/ (%SiO₂ + 2)

NIOSH: 0.05 mg/m³ (suspect carcinogen)

ACGIH: 0.1 mg/m³

PROPERTIES: solid; d 2.65 g/cm³; 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 + PREWEIGHED FILTER (10-mm cyclone, nylon or Higgins-Dewell (HD), and PVC filter, 37-mm, 5-µm) *see sampling section	TECHNIQUE:	INFRARED ABSORPTION SPECTROPHOTOMETRY (IR)
FLOW RATE:	HD cyclone: 2.2 L/min nylon cyclone: 1.7 L/min	ANALYTE:	Quartz
VOL-MIN:	300 L @ 0.1 mg/m ³	WEIGH:	Dust cassette
-MAX:	1000 L	ASH:	Muffle furnace or RF plasma asher
SHIPMENT:	Routine	REDEPOSIT:	0.45-µm acrylic copolymer membrane filter
SAMPLE STABILITY:	Stable	IR:	Scan, 1000 to 650 cm ⁻¹ , absorbance mode with blank filter in reference beam
BLANKS:	2 to 10 field blanks per set	CALIBRATION:	NIST SRM 1878a suspension in 2-propanol
BULK SAMPLE:	Rrequired for OSHA standard calculations; area respirable or settled dust	RANGE:	30 to 250 µg quartz per sample [1]
ACCURACY		ESTIMATED LOD:	10 µg quartz per sample [1]
RANGE STUDIED:	25 to 160 µg/sample [1] (2 mg quartz/m ³ atmosphere)	PRECISION (S_r):	0.098 @ 100 to 500 µg per sample (varies with sample matrix) [1]
BIAS:	Unknown		
OVERALL PRECISION (S_r):	0.13 to 0.22 (varies with sample loading and matrix)		
ACCURACY:	±25.6 to 43.4%		

APPLICABILITY: The working range is 0.03 to 0.25 mg/m³ for a 1000-L sample. The method was specifically developed for respirable coal mine dust samples [1]. The precisions (S_r & S_r) stated above are based on ruggedization data [2]. IR is useful for a simple matrix like coal dust where the interference can be removed. See also discussion of crystalline silica in Chapter R of this volume [3].

INTERFERENCES: Calcite is used as a dusting agent in coal mines and interferes by reacting with quartz during muffle furnace treatment resulting in low quartz assay. Kaolinite is sometimes present in coal dust and interferes by absorbing radiation at the quartz analytical wavelength of 800 cm⁻¹. These interferences are corrected by procedures given in this method. Muscovite does not interfere. Cristobalite and tridymite have absorbance peaks at 800 cm⁻¹. Cristobalite and tridymite have not been detected in coal mine dust.

OTHER METHODS: This is similar to MSHA P-7 which was collaboratively tested [2,4]. Quartz can also be determined by Methods 7500 (XRD) and 7602 (IR). XRD can distinguish the three silica polymorphs and silica interferences can be eliminated by phosphoric acid treatment. Crystalline silica can also be determined by visible absorption spectrophotometry (e.g., Method 7601), but polymorphs cannot 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 [5].

REAGENTS:

1. Quartz* (SRM 1878a, 2950, 2951, 2958), available from Standard Reference Materials Program, Rm. 204, Bldg. 202, National Institute of Standards Technology, Gaithersburg, MD 20899; www.nist.gov.
2. 2-Propanol*, reagent grade.
3. Calibration stock solution, 15 µg/mL. Suspend 7.5 mg of quartz in 2-propanol in a 500-mL volumetric flask and dilute the suspension to the mark with 2-propanol (See CALIBRATION AND QUALITY CONTROL).
4. Kaolinite (Hydrite UF from Georgia Kaolin), for standard samples, 100 µg/mL. Suspend 50 mg of dried kaolinite in a 500-mL volumetric flask with 2-propanol and dilute the suspension to the mark with 2-propanol.

NOTE: This is not required if muffle furnace is used to ash samples (see step 5).

5. Hydrochloric acid solution*. 25% v/v conc. HCl in distilled water. Required if calcite is present and samples are ashed with a muffle furnace.
6. Desiccant (Drierite).
7. Oxygen, purified.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
 - a. Filter: 37-mm diameter, 5.0-µm pore size, polyvinyl chloride filter supported with back up pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
 - b. Cyclone: 10-mm nylon or Higgins-Dewell (HD).
 - c. Sampling head holder: Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
2. Area air sampler: PVC membrane filter, 37-mm, 5-µm pore size in two-piece filter cassette. Sample closed face at 3 L/min
3. Sampling pumps for: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Filters for standards and redeposition, 47-mm diameter, 0.45-µm pore size, vinyl chloride-acrylonitrile copolymer membrane (DM-450 Gelman Sciences, or equivalent).
5. Glass fiber filters, 25-mm diameter, for backup during filtration.
6. Filtration apparatus for redepositing sample after ashing, consisting of fritted support (Millipore XX1002502), side-arm vacuum flask and special funnel similar to Millipore XX1002514 but with an internal diameter of 1.0 cm. The funnel is glass with a bakelite base and should seal to the fritted support to make the fit liquid-tight.**
7. Funnel for treating filters to remove calcite (required only if using a muffle furnace): Millipore XX1002514 with apparatus in item 6 above except with funnel internal diameter ca. 1.6 cm; 0.5-µm pore size PVC filters, 37-mm diameter to recollect residue.**
8. Double-beam infrared spectrophotometer, with sample holders for infrared instrument: metal (preferably steel) plates with a center hole to match the diameter of the sample deposit (1 cm), and small ring magnets to hold the filter in position on the plate.
9. Low-temperature radio frequency asher (LTA) or muffle furnace (600 °C).
10. Ultrasonic bath.
11. Porcelain crucibles with covers, 10-mL.**
12. Beakers, 50-mL.**
13. Analytical balance, 0.01-mg; desiccator cabinet.
14. Magnetic stirrer with thermally insulated top,

EQUIPMENT: - cont.

- and stirring bars.
15. Reagent bottles with ground glass stoppers, 500-mL, and volumetric flasks, 500-mL.**
 16. Tweezers.
 17. Petri dishes, plastic, for 47-mm diameter filters.
 18. Polyethylene wash bottles; metal spatulas.
 19. Serological pipets, various sizes as required.
 20. Lighted viewing box (optional).

** Glassware should be detergent-washed, rinsed thoroughly with distilled or deionized water, and then with 2-propanol, and dried in a dust-free area.

SPECIAL PRECAUTIONS: Avoid inhaling quartz dust [6]. 2-Propanol is flammable. Hydrochloric acid is corrosive and should be handled in a fume hood.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Preweigh each filter to the nearest 0.01 mg.
3. 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 volume of 300 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 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 [7]. 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 [3].

SAMPLE PREPARATION:

4. Reweigh the filters under conditions identical to those before preweighing. The difference is the sample weight, W_s (μg).
5. Ash sample and blank filters by one of the following methods:
 - a. **Low-temperature ashing.**
Using forceps, transfer filter to a 50-mL beaker. Ash 2 h at 300 watts RF power and oxygen flow rate of 75 mL/min following techniques recommended in the instrument manual. After ashing, add 15 mL 2-propanol to each beaker.
 - b. **Muffle furnace ashing.**
 - (1) If the samples contain calcite in concentrations greater than 20% of the total dust loading, wash the filters with acid using the filtration apparatus with the 1.6-cm ID glass funnel. Place a 25-mm glass fiber filter over the frit area, then place a 0.5- μm , 37-mm PVC filter over the glass fiber filter. Clamp down the filter funnel. Add 5 mL 2-propanol and check for leakage.

Remove the sample filter from the cassette. Fold it in half with the collection surface inside, then in quarters. Place the folded filter into the funnel. If necessary, push the filter to the bottom half of the funnel with a glass rod. Add 10 mL HCl solution, then 5 mL 2-propanol. Apply suction and continue until all of the liquid has been removed. Press the folded sample filter onto the surface of the collecting filter if necessary to remove all the liquid. Remove both filters and place in a porcelain crucible. Allow filters to air-dry.

- (2) If acid wash was not required, transfer filter samples and blanks to porcelain crucibles.
 - (3) Loosely cover the crucibles and place in a muffle furnace. Hold for 2 h at 600 °C. After ashing, add several mL 2-propanol to the ash, scrape the crucible to loosen all particles and transfer to a 50-mL beaker. Wash the crucible several times and add wash to beaker. Add 2-propanol to the beaker to bring the volume to ca. 15 mL.
6. Redeposit the sample residue as follows using the filtration apparatus with the 1.0-cm funnel. With a slight vacuum applied, place a 25-mm glass fiber filter on the fritted base. Cut a 47-mm DM-450 filter in half. Superimpose one half over the other, glossy sides down, and place on the glass fiber filter. (The lower half of the DM-450 filter serves as a blank and is used in the reference beam of the infrared spectrometer). Position filter funnel, apply clamp and turn off vacuum. Add several mL 2-propanol to the funnel. Check that the funnel is securely and uniformly clamped. Place sample beakers into ultrasonic bath for at least 30 sec to ensure homogeneous dispersion. Remove a beaker, wipe excess water from the outside, transfer slurry to the filtration funnel and reapply vacuum. During filtration, rinse the beaker twice with 2-propanol to remove all dust and add rinsings to funnel. Control the filtration rate to keep the liquid near the funnel top during rinsing to avoid disturbing the deposit. When the depth of liquid in the funnel reaches ca. 4 cm above the filter, gently rinse the inside of funnel with 2-propanol and complete filtration. Remove the clamp and lift off the funnel, taking care not to disturb and deposit. Release the vacuum. Define the deposit area by marking around the circumference using a pencil or scribe. This is especially important for standards or light-colored samples. Place the DM-450 filter halves in petri dishes and allow to air-dry.

CALIBRATION AND QUALITY CONTROL:

7. Prepare and analyze NIST SRM 1878a standard quartz 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 µm Min-U-Sil, previously used by laboratories throughout the United States and Canada, have been evaluated, and none has been found to be an acceptable alternative to the certified standards cited within this method [3]. Standard reference materials should be corrected for phase purity.
 - NOTE 2: 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) may be useful for preparing working standards at known concentrations.
 - a. Place the flask containing the calibration stock solution in an ultrasonic bath for 30 to 45 min.
 - b. Move the flask to a magnetic stirrer and stir slowly while the flask cools to room temperature. Continue to stir slowly while preparing standards.
 - c. Mount a DM-450 filter in the filtration apparatus in the same manner used to redeposit the samples. Add 5 mL 2-propanol to the funnel. Withdraw an aliquot of the quartz suspension from the center of the flask. Draw liquid to the mark but do not attempt to adjust volume by draining pipet. Carefully wipe the outside of the pipet, then drain the suspension into the filter funnel. Rinse down the inside wall of the pipet with a few mL of 2-propanol, draining the washings into the filter funnel. Apply vacuum to complete the filtration. Prepare quartz standards to cover the range 10 to 250 µg per filter.
 - d. Carry an additional set of these standards and media blanks through steps 5 and 6 to monitor for contamination and losses.
- NOTE: Accuracy depends on obtaining uniform deposition of samples and standards across the filter surface and obtaining reproducible aliquots from the quartz suspension. This requires

some skill. The quartz calibration curve should be prepared before analyzing samples as a check on the analyst's ability to prepare uniform deposits. Repeatability should be <10% on replicate standards with more than 40 µg quartz.

8. Perform an IR scan for each standard filter using the other half of the filter in the reference beam (steps 10 through 12). Construct a calibration graph (absorbance at 800 cm⁻¹ vs. µg quartz per filter). This graph should be linear and pass through the origin.
9. (Only for samples ashed in LTA). Prepare suspensions of at least 5 kaolinite standards in the range 100 to 600 µg per filter. Perform an IR scan of the kaolinite standards from 1000 to 650 cm⁻¹. Draw baselines as described in step 12 and measure the height of the absorbance bands at both 915 and 800 cm⁻¹. Prepare a graph with absorbance at 915 cm⁻¹ as ordinate vs. absorbance at 800 cm⁻¹ as abscissa. Plot a point for each standard. If possible, generate the correction curve data on the same day that coal mine dust samples are analyzed since curve parameters may vary somewhat from day to day. A curve through the points should be linear but will not pass through the origin since the peak at 915 cm⁻¹ is more intense than the peak at 800 cm⁻¹ and small amounts of kaolinite do not interfere with the quartz analysis.

NOTE 1: Kaolinite correction calibration curve is required when samples are ashed in an LTA since kaolinite is not destroyed under these circumstances and has as interfering peak at 800 cm⁻¹ for which a correction must be performed.

NOTE 2: A more detailed discussion of IR peaks is given in the IR section of Chapter R of this volume [3].

NOTE 3: Some training (university or short course) in geology or mineralogy can be useful for the analyst and/or laboratory management. Although most analytical chemists are familiar with the IR technique as applied to organic analyses, mineralogical samples require additional knowledge of geology and mineralogy to correctly interpret crystal structure, matrix interferences and mineral transformation for the laboratory client.

MEASUREMENT:

10. Set appropriate instrument conditions for quantitative analysis.
11. Place the dry DM-450 filter-half containing the dust deposit on a holder. Center the deposit over the hole in the holder and secure the filter with a magnet. (A lighted viewing box facilitates this procedure). Insert the sample into the beam of the spectrophotometer. Place the other half of the DM-450 filter on another holder, secure with a magnet and insert it into the reference beam.
NOTE: For the best precision, the reference filter should be half of the same DM-450 filter which contains the redeposit. However, for routine analysis, the same 2-propanol-treated blank can be used for all filters with the same lot number.
12. Run an infrared scan, in linear absorbance mode from 1000 to 650 cm⁻¹. Draw an appropriate baseline under the absorbance band at 800 cm⁻¹ from ca. 820 to 670 cm⁻¹. Measure and record the absorbance at 800 cm⁻¹, baseline to maximum. If the sample was ashed in an LTA, the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm⁻¹. Draw a baseline under this band from ca. 960⁻¹ to 860 cm⁻¹. Measure and record the absorbance at 915 cm⁻¹, baseline to maximum.
13. Analyze blanks. Check results for contamination.

CALCULATIONS:

14. Correct for kaolinite, if required. Using the sample absorbance at 915 cm⁻¹, refer to the kaolinite curve to find the absorbance at 800 cm⁻¹ due to kaolinite. Subtract this amount from the sample absorbance at 800 cm⁻¹. Use this corrected value to calculate µg quartz in the sample.

15. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} determined in step 12. Determine the weight of quartz, W_q (μg), from the quartz standard curve. Since the deposition area for samples and standards is the same, it is not necessary to correct for area.
16. Calculate the percent quartz by dividing the weight of quartz, W_q (μg), by the total sample weight, W_s (μg).

$$\% \text{quartz} = \frac{W_q}{W_s} \cdot 100$$

EVALUATION OF METHOD:

This method is based MSHA P-7 which was collaboratively tested [2,4]. The testing included a ruggedization step to test the effects of the use of muffle furnace or plasma asher, amount of calcite or kaolinite on the sample, ashing time, pH of solvent to remove calcite, shipment of samples and others. None of these factors was found to have an effect. Results obtained by this method are equivalent to those obtained by Method 7500. A collaborative study of the ruggedized method was performed with 15 laboratories participating [2]. The total errors and interlaboratory and intralaboratory errors were found to be dependent on the types of samples. For samples collected from laboratory-generated aerosols, using a set of matched-flow orifices, the lower and upper limits of the relative standard deviation over the range 60 to 150 μg quartz were:

	<u>Lower</u>	<u>Upper</u>
Total error (RSD)	0.13	0.22
Intralaboratory error	0.07	0.10
Interlaboratory error	0.08	0.14

The lower limit applies to samples containing up to 1 mg coal mine dust with less than 2% kaolinite; the upper limit was found for samples with 2 mg coal mine dust or a lower amount of coal mine dust with more than a few percent kaolinite. The total error increased to 0.36 to 0.40 (lower and upper range) when personal sampling pumps were used to collect the samples. The pump error increased the interlaboratory error. Precision for pure quartz samples is ca. 0.05 in the 100 to 500 μg range [4]. Precision for actual samples is not as good and depends on sample size and ashing technique.

This method is particle size dependent. The particle sizes of the standards and samples should be matched as closely as possible to prevent a bias in the results, which is not correctable with this method. A thorough study of the range of biases has not been done for IR methods.

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