



QUARTZ in Respirable Coal Mine Dust, by IR (Redeposition) 7603

SiO₂

MW: 60.08

CAS: 14808-60-7

RTECS: VV7330000 (quartz)

METHOD: 7603, Issue 4

EVALUATION: FULL

Issue 1: 15 May 1989

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OSHA: 0.05 mg/m³

NIOSH: 0.05 mg/m³; suspect carcinogen

OTHER OELS: [1,2]

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

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING		MEASUREMENT	
SAMPLER:	CYCLONE + PREWEIGHED FILTER (PVC), with conductive filter holder	TECHNIQUE:	INFRARED SPECTROMETRY
FLOW RATE:	~2 to ~4 L/min, specific for the cyclone used	ANALYTE:	Quartz
VOL-MIN:	300 L @ 0.1 mg/m ³	ASHING:	Muffle furnace or RF plasma asher
-MAX:	1000 L (total dust < 4 mg)	REDEPOSIT:	Polypropylene filter (47 mm, 0.45 μm pore size) [3]
SHIPMENT:	Routine	IR DETECTION:	Scan absorbance between 450 cm ⁻¹ and 1000 cm ⁻¹
SAMPLE STABILITY:	Stable	CALIBRATION:	Primary certified reference material quartz, e.g., NIST SRM 1878b, suspended in 2-propanol; or NIST SRM 2950a (quartz on filter)
BLANKS:	3 field blanks minimum per sample set	RANGE:	10 to 500 μg quartz per sample [3-5,7]
ACCURACY		ESTIMATED LOD:	1 μg [3,4]
RANGE STUDIED:	<10 to ~500 μg per sample [3-6]	PRECISION (\bar{S}_r):	0.004 to 0.10 @ 50 to 250 μg per sample [3-6]
BIAS:	Negligible when matrix effects are accounted for		
OVERALL PRECISION ($\hat{S}_{r,T}$):	0.07 to 0.10 [3-7]		
ACCURACY:	±17% to ±33% [5-7]		

APPLICABILITY: The working range is 0.01 to 0.50 mg/m³ for a 1000-L air sample [3,5-7]. The method was originally developed specifically for respirable coal mine dust samples [6,8-10]. IR is useful for a matrix such as coal mine dust, where the interferences can be predictably removed and minimized.

INTERFERENCES: Amorphous silica, kaolinite, muscovite, talc, albite, vermiculite and other minerals that absorb IR radiation in the 800 cm⁻¹ region are potential interferences to RCS measurement [11,12] [Table 1]. Potentially interfering silicates can be removed using a phosphoric acid cleanup procedure [13]. Calcite at >20% dust loading can negatively interfere by reacting with quartz during muffle ashing [10,14]. The sample preparation procedures described in this method enable minimization of potential interferences.

OTHER METHODS: NIOSH Method 7602 describes sample preparation and IR measurement of respirable crystalline silica (RCS) by means of a KBr pellet [15]. X-ray diffraction (e.g., NIOSH Method 7500 [15]) is a complementary method for quartz measurement by IR. MSHA Method P-7 [6] is an equivalent IR method for respirable quartz. An international voluntary consensus standard describing the measurement of RCS by IR spectrometry, ASTM D7439, has been promulgated [16].

REAGENTS:

1. Quartz primary certified reference material (CRM); e.g., NIST SRM 1878b or SRM 2950a [17].
2. Kaolinite CRM; e.g., material meeting requirements from USP#
3. Deionized water, ≥ 18 M Ω -cm resistivity.
4. 2-Propanol, reagent grade.
5. Ethanol, 95%, for cleaning of sampling equipment.*
6. Hydrochloric acid* (HCl) solution, 25% v/v: Add 25 mL conc. HCl (37% w/w) to 50 mL with deionized water, cool, and bring to 100 mL with deionized water.
NOTE: Required if calcite is present and samples are prepared using a muffle furnace.
7. Calibration stock solution (quartz suspension in 2-propanol), 15 mg/L: Accurately weigh 7.5 mg of quartz and add to about 400 mL of 2-propanol in a 500-mL volumetric flask. Bring the suspension to the mark with 2-propanol.
8. Kaolinite suspension, 100 mg/mL: Accurately weigh 50 mg of dried kaolinite and add to about 400 mL of 2-propanol in a 500-mL volumetric flask. Bring the suspension to the mark with 2-propanol.
NOTE: Not required if muffle furnace used for sample ashing.
9. Desiccant.
10. Oxygen, purified.

#United States Pharmacopeia Convention

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. Filters, 37-mm dia., 5- μ m pore size, polyvinyl chloride (PVC), supported with backup pad or screen in 2-piece, conductive / static-dissipative filter holder.
 - b. Cyclone, respirable, designed to operate at a flow rate of ≈ 2 or ≈ 4 L/min, specific for each sampling device.
 - c. Sampling head holder, for keeping the cassette, cyclone and coupler tightly together so that air enters only through cyclone inlet.
2. Personal sampling pumps, for sample collection at ≈ 2 or ≈ 4 L/min.
3. Infrared spectrometer, double-beam dispersive or Fourier transform device, with 4 cm^{-1} resolution or better.
4. Filtration apparatus (for redepositing sample after ashing), consisting of fritted support, side-arm vacuum flask and glass filtration funnel with bakelite base, 1.0 cm internal diameter. The base should seal tightly to the fritted support to prevent leakage.
5. Filters for standards and redeposition, 47-mm, 0.45- μ m pore size, polypropylene (PP).
6. Glass fiber filters, 25-mm dia., for backup during filtration.
7. Filtration funnel for treating filters (required only if using a muffle furnace): same as in 6. above except with funnel i.d. about 1.6 cm and with 0.5- μ m pore size 37-mm dia. PVC filters to recollect residue.
8. Low-temperature (RF plasma) asher and aluminum weighing pan, or muffle furnace and 10-mL porcelain crucibles (with covers).
9. Analytical balance, capable of weighing to the nearest 0.001 mg.
10. Ultrasonic bath.
11. Desiccator.
12. Beakers, 50-mL.
13. Magnetic stirrer with insulated top.
14. Volumetric flasks with stoppers, 500-mL.
15. Tweezers and metal spatulas.
16. Petri dishes, for 47-mm dia. filters.
17. Wash bottles.
18. Pipets, various sizes as required.

SPECIAL PRECAUTIONS: Wear appropriate personal protection during sampling activities, sample preparation and analysis. It is essential that suitable gloves, eye protection, laboratory coat, etc., be used, especially when working with concentrated acids. Ethanol and 2-propanol are flammable. Avoid exposure by inhalation of silica dust or acid fumes. Perform sample preparation and analysis in a clean, well-ventilated area that is well removed from any possible contamination. Any skin affected by exposure to acids must be immediately washed with plenty of water.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line. Use conductive filter holders.
2. Pre-weigh each filter to the nearest 0.01 mg.
3. Sample at ≈ 2 L/min [18] or ≈ 4 L/min [5] using a pump set at a specific flow rate for a selected cyclone, designed to collect the respirable aerosol fraction (in accordance with ISO 7708[19]), for a total sample size of 400 to 1000 L. Take care not to overload 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 more than a horizontal orientation may deposit oversized material from the cyclone body onto the filter.

NOTE 2: Higher sampling flow rates may be suitable for certain sampler designs [20].

4. After collection of samples, remove the filter holders from the cyclones. Seal the filter holders (cassettes) and transport them to the laboratory in a container designed to prevent damage in transit.

SAMPLE PREPARATION:

5. Remove the filters from filter holders and, after preconditioning to ambient conditions, re-weigh the filters to the nearest 0.01 mg; the difference is the sample weight, W_s (μg).
6. Use one of the following methods to prepare samples and blanks:
 - a. Low-temperature (RF plasma) asher: Transfer the weighed filters to clean 50-mL beakers. Place the beakers in the low-temperature asher so that sample exposure to the plasma is optimized. Ash the samples for 2 h at 300 W RF power and oxygen flow rate of 75 mL/min, according to manufacturer's instructions. Carefully bring the asher to atmospheric pressure, remove the beakers, and add 15 mL 2-propanol to each beaker.
 - b. Muffle furnace: For samples expected to contain a significant amount of calcite (>20% of the total dust loading), wash filters with 25% v/v HCl using the filtration apparatus with the 1.6-cm i.d. glass funnel. For other samples, proceed to step 6.b.ii.
 - i. Place a 25-mm glass fiber filter over the frit area of the filtration funnel, then place a 0.45- μm pore size, 37-mm dia. PP filter atop the glass fiber filter. Clamp the funnel over the frit and ensure that there is no leakage. Using tweezers and gloved hands, take the weighed sample filter and fold it in half with the collection surface inside, then fold again into quarters, and place the folded filter into the funnel. Add 10 mL of 25% HCl (v/v), then 5 mL of 2-propanol; allow to stand for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel. Press the folded sample filter onto the surface of the collection filter if necessary to remove all liquid. Release vacuum, remove both filters and place in a porcelain crucible. Allow to air-dry.
 - ii. Place filter samples and blanks in porcelain crucibles, loosely cover, and ash in muffle furnace for 2 h at 600 °C (800 °C if graphite present). Allow to cool to room temperature.
 - iii. Add ~ 3 mL 2-propanol to the ash within each crucible, scrape the crucible to loosen all particles, and quantitatively transfer to contents to a 50-mL beaker. Wash the crucible several times with 2-propanol and add the wash to the beaker. Add 2-propanol to the beaker to bring the volume to ~ 15 mL.
7. Redeposit the sample residue as follows, using the filtration apparatus with the 1.0 cm dia. funnel. With a slight vacuum applied, place a 25-mm glass fiber filter on the fritted base. Cut a 47-mm 0.45- μm PP filter in half. Superimpose one half over the other, glossy sides down, and place on the

glass fiber filter. (The lower half of the PP filter serves as a blank for use in the reference beam of the IR spectrometer.) Position the filter funnel, apply clamp, turn off vacuum and ensure that there is no leakage. Place sample beakers from step 6.b.iii into ultrasonic bath for at least 30 sec to ensure homogeneous dispersion. Remove each beaker, wipe off excess water from the outside of the beaker, and transfer the slurry to the filtration funnel. Reapply vacuum and, during filtration, rinse the beaker twice with 2-propanol to ensure quantitative transfer of entire contents to the funnel. Control the filtration rate to keep the liquid near the top of the funnel during rinsing to avoid disturbing the deposit. When the depth of liquid in the funnel reaches about 4 cm above the filter, gently rinse the inside of the funnel with 2-propanol and complete filtration. Remove clamp and funnel, taking care not to disturb the 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 PP filter halves in Petri dishes and allow to air dry.

CALIBRATION AND QUALITY CONTROL:

8. Prepare at least 5 working standard quartz filters. Calibration standards shall be prepared from primary CRMs of known purity, particle size range and homogeneity.

NOTE: Suitable quartz standards include primary reference materials such as NIST SRM 1878b or 2950; the use of secondary reference materials as calibration standards is not appropriate for IR measurement [14].

- a. Place the flask containing the calibration stock solution in an ultrasonic bath for 30-45 min.
- b. Move the flask to a magnetic stirrer and stir slowly while the flask cools to room temperature. Continue slow stirring while preparing calibration standards.
- c. Mount a PP filter in the filtration apparatus in the same manner used to redeposit the samples. Add 5 mL of 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 funnel. Apply vacuum to complete the filtration. Prepare quartz standards in this manner to cover the range 10 to 250 μg per filter.
- d. Carry an additional set of these calibration standards and media blanks through steps 6 and 7 to monitor for contamination and losses.

NOTE: Accuracy depends on obtaining uniform deposition of samples and calibration standards across the filter surface and obtaining reproducible aliquots from the quartz suspension. This requires skill and practice. 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 calibration standards with >40 μg of quartz.

9. Perform IR scans for each standard filter using the other half of the filter in the reference beam (see Measurement section). Construct a calibration graph of absorbance at 800 cm^{-1} vs. μg of quartz per filter. The plot should be linear and pass through the origin.
10. If samples were low-temperature ashed and kaolinite is known to be present in the matrix of the collected samples, prepare at least five different loadings of PP filters containing 100 to 600 μg of kaolinite. Measure the IR absorbance of kaolinite standards from 1000 cm^{-1} to 650 cm^{-1} . Prepare a graph with absorbance at 915 cm^{-1} as ordinate vs. absorbance at 800 cm^{-1} as abscissa. Use the relationship between the quartz and kaolinite peak to correct the absorbance value at 800 cm^{-1} samples containing kaolinite [20].
11. Carry media blanks and filters spiked with known amounts of quartz through the sample preparation procedures to monitor for contamination and losses.

NOTE: Knowledge of and training in geochemistry and mineralogy is strongly recommended for users of this method. Although many analytical chemists are familiar with IR spectroscopy (e.g., as applied to organic analysis), mineralogical samples such as those containing RCS require

additional knowledge of geochemistry and mineralogy to correctly interpret IR spectra and account for matrix interferences and mineral transformations.

MEASUREMENT:

12. Set the infrared spectrometer to double-beam absorbance mode and to the appropriate settings for quantitative analysis. For each IR scan, place a PP sample filter half in the sample beam and a PP blank filter half in the reference beam, and obtain a spectrum at 4 cm^{-1} resolution or better from 450 cm^{-1} to 1000 cm^{-1} . For each PP filter sample, center the IR beam on filter deposit.
13. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from approximately 820 to 670 cm^{-1} . Measure the absorbance from the 800 cm^{-1} peak maximum to baseline in absorbance units.
NOTE: If the peak at 800 cm^{-1} is small, expand the ordinate to enhance the peak height.
14. If the sample was ashed at low temperature, the presence of kaolinite will be indicated by an absorption band with maximum at 915 cm^{-1} . Draw an appropriate baseline under the absorbance band at 915 cm^{-1} from approximately 960 to 860 cm^{-1} . Measure the absorbance from the 915 cm^{-1} peak maximum to baseline.
15. Analyze blanks and, if necessary, correct baseline.

CALCULATIONS:

16. To correct for the presence of kaolinite (if necessary), use the measured absorbance at 915 cm^{-1} and refer to the kaolinite curve to establish the corrected absorbance for quartz at 800 cm^{-1} [21]. Use this corrected absorbance value at 800 cm^{-1} in calculating the airborne quartz concentration.
17. If correction for kaolinite is not required, use the measured (uncorrected) absorbance at 800 cm^{-1} to determine the weight (W_s , μg) quartz from the calibration graph.
18. From the weight of quartz (W_s , μg), calculate its concentration, C (mg/m^3), in the volume of air sampled, V (L):

$$C = [W_s / V], \text{mg}/\text{m}^3$$

19. If percent quartz (%Q) is of interest, divide the weight of quartz, W_s (μg), by the total sample weight, W_t (μg):

$$\%Q = [W_s / W_t] \times 100$$

EVALUATION OF METHOD:

The method is based on MSHA method P-7, which was collaboratively tested [4] and optimized [6]. Interlaboratory evaluation included a ruggedization step to test the effects of the use of muffle furnace or plasma asher, amount of calcite or kaolinite in the sample, ashing time, pH of solvent used to remove calcite, shipment of samples, and other factors. None of these contributions was found to have a statistically significant effect. Filter collection has been carried out using respirable cyclone samplers with flow rate $\approx 2\text{ L}/\text{min}$ [4] and $\approx 4\text{ L}/\text{min}$ [5], with sampling volumes ranging from 300 to 1000 L; analysis was subsequently carried out using the redeposition method. Applicable analytical ranges were from $3\text{ }\mu\text{g}$ [5] to $500\text{ }\mu\text{g}$ quartz [4,6] per sample, with estimated method detection limits (MDLs) of $1\text{-}5\text{ }\mu\text{g}$ or even less [3]. Reported precision estimates, in terms of relative standard deviation, were 0.10 or below at quartz mass per sample of $20\text{-}400\text{ }\mu\text{g}$ [3-6]. The IR redeposition method has been used extensively to measure the quartz content of respirable dusts collected in coal mines [3,8-10,21,22]. Laboratories using the IR redeposition method have performed successfully in interlaboratory proficiency analytical testing programs [7, 23, 24].

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Table 1. Minerals potentially encountered and their characteristic IR bands (450-1000 cm⁻¹)

Mineral	Major/Interfering Peaks, cm⁻¹	Identifying Peaks, cm⁻¹
Quartz	800, 780	694, 512, 467
Cristobalite	798	623, 490
Tridymite	789	617, 476
Amorphous silica	800	464
Kaolinite	795, 754	915, 547, 474
Muscovite	800, 750	535, 481
Mullite	837, 748	556, 468
Pyrophyllite	830, 814	948, 477, 457
Albite	788, 746	726, 652, 598, 470
Montmorillonite	797	918, 668, 526, 470
Daphnite	798, 771	667, 610, 539, 467
Anorthite	760, 730	577, 538, 481
Orthoclase	765, 745, 730	645, 593, 540
Talc	797, 778	668, 641, 620
Vermiculite	810, 755	685, 510