SILICA, Respirable Crystalline, by IR (KBr pellet)

7602

SiO_2	MW: 60.08	CAS:	14808-60-7 14464-46-1 15468-32-3	RTECS:	VV7330000 (quartz) VV7325000 (cristobalite) VV335000 (tridymite)

METHOD: 7602, Issue 4

EVALUATION: FULL

Issue 1: 15 February 1984
Issue 4: 25 July 2017

OSHA: 0.05 mg/m^3
NIOSH: 0.05 mg/m^3; carcinogens
OTHER OELS: [1,2]

PROPERTIES: solid; d 2.65 g/cm^3; crystalline transformation: α-quartz to β-quartz @ 573 °C; quartz to tridymite @ 867 °C; tridymite to cristobalite @ 1470 °C

SYNONYMS: free crystalline silica; silicon dioxide

SAMPLING

SAMPLER:	CYCLONE + PRE-WEIGHED FILTER (PVC), with conductive filter holder
FLOW RATE:	~2 to ~4 L/min, specific for the cyclone used
VOL-MIN:	400 L
-MAX:	1000 L (total dust < 4 mg)
SHIPMENT:	Routine
SAMPLE STABILITY:	Stable
BLANKS:	3 field blanks minimum per sample set

ACCURACY

RANGE STUDIED:	5 to >160 µg
BIAS:	Varies depending on matrix effects
OVERALL PRECISION ($\hat{S}_{rT}$):	0.18 [3]
ACCURACY:	±19% at ≈40-160 µg per sample; ±36% at ≈15 µg per sample [4]

MEASUREMENT

TECHNIQUE:	INFRARED SPECTROMETRY
ANALYTE:	Quartz / Cristobalite
ASHING:	Muffle furnace or RF plasma asher
PELLET:	Mix residue with KBr; press 13-mm pellet
IR DETECTION:	Scan absorbance between 400 cm^{-1} and 1000 cm^{-1}
CALIBRATION:	Certified reference material (CRM) respirable crystalline silica (RCS) quartz & cristobalite; e.g., NIST SRM 1878b quartz, NIST 1879a cristobalite, and/or other RCS CRMs; diluted in KBr and pressed into 13-mm pellet
RANGE:	10 to >160 µg
ESTIMATED LOD:	5 µg
PRECISION ($\bar{S}_r$):	< 0.15 @ 30 µg per sample

APPLICABILITY: The working range is 0.025 to 0.4 mg/m^3 for a 400-L air sample or 0.02 to 0.25 mg/m^3 for a 1000-L air sample. Quartz and cristobalite have a major IR absorbance band at ≈800 cm^{-1} and can be measured together if present in samples; tridymite can also be measured by IR, but its presence is rare in workplaces [5-9].

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 [5,10] [Table 1]. Potentially interfering silicates can be removed using a phosphoric acid cleanup procedure [11]. Calcite at >20% dust loading can negatively interfere by reacting with quartz during muffle ashing [11, 12]. The sample preparation procedures described in this method enable minimization of interferences.

OTHER METHODS: NIOSH Method 7603 describes IR measurement of respirable crystalline silica (RCS) after redeposition onto a filter for analysis (vs. use of a KBr pellet) [13]. X-ray diffraction (e.g., NIOSH Method 7500 [13]) is a complementary method for RCS measurement. An international voluntary consensus standard describing the measurement of RCS by IR spectrometry, ASTM D7439, has been promulgated [14].

REAGENTS:

1. Respirable crystalline silica (RCS) primary certified reference materials (CRMs); e.g., NIST SRM 1878b (quartz), NIST SRM 1879a (cristobalite) [15].
2. Potassium bromide (KBr), IR quality.
3. Kaolinite (kaolin) CRM.
4. Deionized water, ≥18 MΩ-cm resistivity.
5. 2-Propanol, reagent grade.
6. Ethanol, 95%, for cleaning of sample handling equipment.*
7. Hydrochloric acid (HCl), 9% w/w.* Add 25 mL conc. HCl (37% w/w) to 50 mL of deionized water, cool, and bring to 100 mL with deionized water.
8. Calibration stock standard, 0.5% w/w. Accurately weigh and thoroughly mix 5 g KBr (dried overnight at 110 °C) with 25 mg quartz. Store in a bottle in a desiccator.

*See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
   a. Filter, 37-mm dia., 5-µm 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 RCS 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. Laboratory press (10 tons pressure), for preparing KBr pellets, with evacuable 13-mm KBr pellet die.
5. Vacuum pump, for connecting to laboratory press.
6. Low-temperature (RF plasma) asher and aluminum weighing pan, or muffle furnace and porcelain crucibles.
7. Analytical balance, capable of weighing to the nearest 0.001 mg.
8. Mortar and pestle, 50-mm agate or mullite
9. Metal microspatula
10. Non-serrate, non-magnetic forceps
11. Desiccator
12. Camel’s hair brush
13. Glassine paper / weighing boats
14. Membrane filtration apparatus (47-mm)
15. Laboratory oven

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. Note that KBr is incompatible with strong 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 a conductive filter holder.
2. Sample at ≈2 L/min [16] or ≈4 L/min [17] using a pump set at a specific flow rate for the selected cyclone, designed to collect the respirable aerosol fraction (in accordance with ISO 7708[18]), 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 [19].
3. 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:

4. Use one of the following methods to prepare samples and blanks:
   a. Low-temperature (RF plasma) asher: Remove the filters from filter holders and place them in clean, labelled aluminum dishes. Place the dishes in the low-temperature asher so that sample exposure to the plasma is optimized. Ash the samples according to manufacturer's instructions. Carefully bring the asher to atmospheric pressure and remove the dishes.
   b. Muffle furnace: For samples expected to contain a significant amount of calcite (>20% of the total dust loading), wash filters with 9% w/w HCl per procedure in 4.b.i. For other samples, proceed to step 4.b.ii.
      i. Place a 0.5-µm pore size, 47-mm dia. PVC filter in the filtration apparatus. Remove the 37-mm dia. sample filter from the filter holder and center atop the 47-mm PVC filter. Clamp a funnel over the frit so that the dust deposit on the filter is completely exposed to rinsates. Add 10 mL of 9% HCl and 5 mL of 2-propanol; allow to stand for 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel. Wash with three successive 10-mL portions of deionized water. Release vacuum.
      ii. Place 37-mm 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.
5. Add approximately 300 mg KBr, weighed to the nearest 0.1 mg and dried overnight at 110 °C, directly to each sample. Mix the sample residue (remaining from the above ashing procedure) with KBr using a pestle and grind / homogenize the mixture with mortar and pestle. Quantitatively transfer the mixture to a 13-mm evacuable pellet die using glassine paper and camel's hair brush. Place the die into the laboratory press and apply requisite pressure to prepare the sample KBr pellet. Weigh the finished pellet to the nearest 0.1 mg and calculate the ratio of the weight of the finished pellet to the weight of KBr initially added. Clean sample handling equipment with ethanol between samples.

CALIBRATION AND QUALITY CONTROL:

6. Prepare at least 5 working standard KBr pellets. Calibration standards shall be prepared from primary RCS CRMs.

   NOTE: Suitable RCS standards include primary reference materials such as NIST SRMs 1878b (quartz) and 1879a (cristobalite) [15]; the use of secondary reference materials as calibration standards is not appropriate for IR measurements [12, 20].
   a. Weigh, to the nearest 0.001 mg, portions of primary CRMs containing 10 to 200 µg RCS of material.
   b. Add an accurately weighed (to the nearest 0.001 mg) 300 mg portion of KBr. Prepare KBr pellet samples as in Step 5. Compute the ratio of the weight of finished pellet / weight of solids added.
   c. Measure the absorbance at 800 cm^{-1} for each KBr pellet calibration standard following the analytical procedure below (Step 9). Plot the absorbance vs. mass of SiO_2 (µg).

7. If samples were low-temperature ashed (Step 4.a.) and kaolinite is known to be present in the matrix of the collected samples, prepare at least five different KBr pellets containing 100 to 600 µg of kaolinite. Measure the absorbance at 800 cm^{-1} (RCS) and at 915 cm^{-1} (kaolinite). Use the relationship between the RCS and kaolinite peak to correct the absorbance value at 800 cm^{-1} samples containing kaolinite [21].
8. Carry media blanks and filters spiked with known amounts of RCS (e.g., quartz) through the sample preparation procedures (Steps 4 and 5) 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:

9. Set the infrared spectrometer to absorbance mode and to the appropriate settings for quantitative analysis. For each IR scan, place a KBr pellet in the sample holder and obtain a spectrum at 4 cm^{-1} resolution or better from 400 cm^{-1} to 1000 cm^{-1}. Rotate the KBr pellet 45° and scan again. Repeat twice more until 4 scans have been obtained. 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. Average the four absorbance values for each KBr pellet sample.
   NOTE: If the peak at 800 cm^{-1} is small, expand the ordinate to enhance the peak height.
10. If the sample was ashed at low temperature (Step 4.a.), 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.

CALCULATIONS:

11. To correct for the presence of kaolinite (if necessary), use the measured absorbance at 915 cm^{-1} (Step 10) and refer to the kaolinite curve (Step 6) to establish the corrected absorbance for RCS at 800 cm^{-1}. Use this corrected RCS absorbance value in Step 13.
12. If correction for kaolinite is not required, use the measured (uncorrected) absorbance at 800 cm^{-1} to determine the weight (W_s, µg) of RCS (e.g., quartz) from the calibration graph.
13. From the weight of RCS (W_s, µg), calculate its concentration, C (mg/m^3), in the volume of air sampled, V (L):

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

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

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

EVALUATION OF METHOD:

From various experimental studies, analytical figures of merit for the KBr pellet IR method for RCS have been summarized in Ref. [14]. Filter collection was carried out using respirable cyclone samplers with flow rate ≈2 L/min, with sampling volumes ranging from 300 to 1000 L. Following sample ashing with a plasma asher or muffle furnace, the remaining material was homogenized with KBr and pressed into a KBr pellet. IR spectrometric measurements were then carried out on the as-prepared KBr discs. By comparison of sample IR response to the signal from similarly-prepared CRM quartz standards, and with interference correction [21], the RCS content was measured. Applicable analytical ranges were from 3 to 900 µg per sample, with estimated method detection limits (MDLs) of 5 µg or less. Reported precision estimates, in terms of relative standard deviation, were 0.15 or below at RCS mass per sample of 30 µg. To further optimize the method, matching CRM particle size distribution to that of RCS samples [20] has been applied to minimize the effect of particle size on the IR response. The KBr pellet IR method has been used to measure the crystalline silica content of respirable dusts collected at various workplaces, including coal mines [7,8,22], construction sites [23], granite quarries [9] and gold mines [24]. Laboratories using the KBr disc method have performed successfully in interlaboratory proficiency analytical testing programs [3,25,26].

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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