

SILICA, CRYSTALLINE by IR (KBr pellet)

7602

SiO₂

MW: 60.08

CAS:14808-60-7

14464-46-1

15468-32-3

RTECS: VV7330000 (quartz)

VV7325000 (cristobalite)

VV335000 (tridymite)

METHOD: 7602, Issue 3

EVALUATION: PARTIAL

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OSHA : quartz (respirable): 10 mg/ m³ / (% SiO₂ + 2);
cristobalite and tridymite (respirable): 1/2 the above
NIOSH: 0.05 mg/m³ ; carcinogens
ACGIH: quartz (respirable) 0.1 mg/m³ cristobalite and
tridymite (respirable) 0.05 mg/m₃

PROPERTIES: solid; d 2.65 g/cm³; crystalline
transformation: 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 + FILTER (10-mm nylon or Higgins-Dewell (HD), and PVC filter, 37-mm, 5-µm) *see sampling section	TECHNIQUE:	INFRARED ABSORPTION SPECTROPHOTOMETRY
FLOW RATE:	Nylon cyclone: 1.7L/min HD cyclone: 2.2 L/min	ANALYTE:	Quartz
VOL-MIN: 400 L		ASH:	Muffle furnace or RF plasma asher
-MAX: 800 L		PELLET:	Mix residue with KBr; press 13-mm pellet
SHIPMENT:	Routine	IR:	Scan absorbance from 1000 to 600 cm ⁻¹
SAMPLE STABILITY:	Stable	CALIBRATION:	NIST SRM 1878a quartz, NIST SRM 1879a cristobalite, USGS 210-75-0043 tridymite diluted in KBr
BLANKS:	2 to 10 field blanks per set	RANGE:	10 to 160 µg quartz
BULK SAMPLE:	High volume or settled dust to identify interferences	ESTIMATED LOD:	5 µg quartz
PRECISION (S.):		< 0.15 @ 30 µg quartz per sample, in coal dust [1]	
ACCURACY			
RANGE STUDIED:	Not studied		
BIAS:	Not determined		
OVERALL PRECISION (Ŝ_r):	Not determined		
ACCURACY:	Not determined		

APPLICABILITY: The working range is 0.025 to 0.4 mg/m³ for a 400-L air sample. Cristobalite and tridymite also have major absorbance peaks at 800 cm⁻¹ which can be used for their determination [1-6]. IR methods can quantify quartz, cristobalite and tridymite if amorphous silica and silicates are not present in large amounts. However, sensitivity is reduced if multiple polymorphs are present and secondary peaks must be used. A potential for bias exists when correcting for matrix absorption effects, with an increasing risk of bias at lower quartz concentrations. See also discussion of crystalline silica in Chapter R of this volume [7].

INTERFERENCES: Amorphous silica, calcite, cristobalite, kaolinite and tridymite interfere; see APPENDIX.

OTHER METHODS: This is P&CAM 110 in a revised format [1]. It is similar to Method 7603, except for sample preparation (KBr pellet vs. redeposition). XRD (method 7500) 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 [8].

REAGENTS:

1. Silica Standards.
 - a. Quartz* (SRMs 1878a, 2950, 2951, 2958) and Cristobalite* (SRMs 1879a, 2960, 2957), available from Standard Reference Materials Program, Rm 204, Bldg. 202, National Institute of Standards and Technology, Gaithersburg, MD 20899; www.nist.gov.
 - b. Tridymite* (210-75-0043), available from U.S. Geological Survey, PO Box 25046, MS 973, Denver, CO 80225.
2. Potassium bromide (KBr), infrared quality.
3. Ethanol, 95% for cleaning sample handling equipment.*
4. Hydrochloric acid, 9% w/w.* Add 25 mL conc. HCl (37% w/w) to 70 mL with deionized water, cool, and bring to 100mL with deionized water.
5. 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 diameter, 5.0- μ m pore size, polyvinyl chloride filter supported with backup 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- μ m pore size in two piece filter cassette. Sample closed-faced 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. Infrared spectrophotometer; laboratory press for preparing KBr pellets; 13-mm KBr pellet die (evacuatable).
5. Low-temperature (RF Plasma) asher and aluminum weighing pan or muffle furnace and porcelain crucibles.
6. Mortar and pestle, 50-mm agate or mullite metal microspatula; non-serrate, non-magnetic forceps; desiccator, camel's hair brush, glassine paper.
7. Analytical balance (0.001 mg) for preparing standards.
8. Membrane filtration apparatus, 37-mm.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [9]. Ethanol is flammable. Keep away from flames. Use personal protective equipment to prevent contact of acids with the skin. Concentrated acids are corrosive.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at $1.7 \pm 5\%$ L/min with nylon cyclone, $2.2 \pm 5\%$ with HD cyclone, or $2.5 \pm 5\%$ with AI cyclone for a total sample size of 400 to 800 L. Do not exceed 2 mg total 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 more 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 [10]. 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 [7].

SAMPLE PREPARATION:

3. Use one of the following methods to ash samples and blanks:
 - a. Low temperature (RF Plasma) asher: Place the filters in labelled aluminum dishes (previously rinsed with distilled water, followed by ethanol, and air dried). Place the dishes in the low temperature asher so that sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. Carefully bring asher to atmospheric pressure and remove the dishes.
 - b. Muffle furnace: For samples containing a significant amount of calcite (> 20% of the total dust loading), wash filters with 9% w/w hydrochloric acid. Other samples proceed to step 3.b.ii.
 - i. Place a 0.5- μ m, 47-mm PVC filter in the filtration apparatus. Remove sample filter from cassette and center on top of first filter. Clamp funnel over the frit so that dust deposit is completely exposed. Add 10 mL 9% w/w HCl and 5 mL 2-propanol; allow to stand 5 min. Apply vacuum and slowly aspirate the acid and alcohol in the funnel. Wash with three successive 10-mL portions of distilled water. Release vacuum.
 - 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 is present).
4. Add approximately 300 mg KBr, weighed to 0.1 mg and dried overnight at 110 °C, directly to each sample. Mix the sample ash and KBr thoroughly with a pestle. Transfer to mortar to complete mixing if necessary. Transfer the mixture to a 13-mm evacuable pellet die using glassine paper and camel's hair brush. Press a pellet using standard technique. Weigh the finished pellet to 0.1 mg. Calculate the ratio (weight of finished pellet/weight KBr initially added); it is usually about 0.98. Clean sample handling equipment with ethanol between samples.

NOTE: A low relative humidity environment will facilitate sample handling when using KBr.

CALIBRATION AND QUALITY CONTROL:

5. Prepare at least 5 working standard pellets:

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 μ m 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 [7]. 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.

 - a. Weigh, to 0.001 mg, portions of NIST α -quartz SRM 1878a, NIST cristobalite SRM 1879a, USGS tridymite 210-75-00473 containing 10 to 200 μ g standard.
 - b. Add an accurately-weighed 300 mg KBr portion. Proceed as in step 4.
 - c. Calculate the ratio (weight of finished pellet/weight of solids added); usually about 0.98.
 - d. Determine the absorbance at 800 cm^{-1} for each standard pellet following the analytical procedure (step 8). Plot absorbances vs. μ g SiO_2 .
6. If samples were low temperature ashed (step 3.a.) and kaolinite is present, prepare pellets containing 100 to 600 μ g kaolinite. Determine the absorbance at 800 cm^{-1} and at 915 cm^{-1} as abscissa. Prepare at least five different kaolinite concentrations. Use this curve to correct the absorbance value at 800 cm^{-1} for any sample containing kaolinite.
7. Carry media blanks and filters spiked with known amounts of quartz through the sample preparation procedures (steps 3 and 4) to monitor for contamination and losses.

NOTE: 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:

8. Set the infrared spectrophotometer to absorbance mode and to the appropriate settings for quantitative analysis. Scan the pellet from 1000 cm^{-1} to 600 cm^{-1} . Rotate the pellet 45° and scan this diameter. Repeat twice more until 4 scans have been obtained. If the peak at 800 cm^{-1} is small, use 5X ordinate expansion to enhance the peak height. Draw an appropriate baseline under the absorbance band at 800 cm^{-1} from approximately 820 to 670 cm^{-1} . Measure the absorbance at 800 cm^{-1} from maximum to baseline in absorbance units. Average the four values for each sample.
9. If the sample was ashed at low temperature (step 3.a), the presence of kaolinite will be indicated by an absorption band with a maximum at 915 cm^{-1} . Draw an appropriate baseline under this band from approximately 960 to 860 cm^{-1} and measure the absorbance at 915 cm^{-1} from this baseline to the maximum.

CALCULATIONS:

10. To correct for kaolinite, determine the sample absorbance at 915 cm^{-1} (step 9) and refer to the kaolinite curve (step 6) to find the absorbance at 800 cm^{-1} . Use this corrected value in step 11.
11. If correction for kaolinite is not required, use the absorbance at 800 cm^{-1} to find the weight of quartz, W_q (μg), from the calibration graph.
12. Calculate the concentration of silica, C (mg/m^3), in the volume of air sampled, V (L):

$$C = \frac{W_q}{V}, \text{mg} / \text{m}^3$$

13. If percent quartz, % Q, is required, divide the weight of quartz, W_q (μg), by the total sample weight, W_s (μg):

$$\%Q = \frac{W_q}{W_s} \cdot 100$$

EVALUATION OF METHOD:

This method is based on the well-characterized infrared method [1]. This method is particle size dependent. A mismatch of standards and sample particle sizes will result in an uncorrectable bias. Only NIST-certified standard reference materials (SRM) 1878a and 1879a and USGS 210-75-0043 have been found to have sufficient purity, sample-to-sample homogeneity in crystalline silica content and particle size necessary to ensure that results are similar to results obtained by other laboratories using other methods. A thorough study of the range of biases in IR methods has not been done.

REFERENCES:

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APPENDIX A:

INTERFERENCES

Quartz and cristobalite can be determined in each other's presence by the use of less sensitive bands at 695 cm^{-1} (quartz) and 625 cm^{-1} (cristobalite). Tridymite can only be determined in the absence of the other two polymorphs; it is rarely encountered in industrial hygiene samples. Interfering silicates can be removed using a phosphoric acid cleanup procedure [2].

Cristobalite and tridymite interfere positively at the 800 cm^{-1} peak, although they are rarely present in industrial hygiene samples. Kaolinite, a common component of coal, can interfere when RF plasma ashing is used to remove the collection filter, if it is present in sufficient quantity. A correction procedure is outlined in the method (steps 6 and 10). Calcite, at greater than 20% of the total dust loadings, can interfere by reacting with the quartz during muffle ashing. A procedure for its removal is given (step 3.b). Amorphous silica may interfere if present in large amounts. This interference can be minimized by accounting for its broad absorbance band when drawing the baseline.

Quartz is a common component of soil, rocks, sand, mortar, cement, fluxes, abrasives, glass, porcelain, paints and brick. Cristobalite is less common and found in volcanic rocks and soils, and can be formed in high temperature processes such as foundry processes, calcining diatomaceous earth, brick manufacturing, ceramic manufacturing and silicon carbide production. Tridymite is rarely encountered, but is present in some volcanic rocks and soils.

APPENDIX B:

DETERMINATION OF QUARTZ IN BULK SAMPLES

Additional equipment needed: Drying oven
 Wilks Mini-Press, or other pellet press
 Min-U-Sil 30

1. Homogenize the sample if necessary (e.g., by grinding using a large mortar and pestle) and dry it (e.g., in a vacuum oven at 110 °C for 2-4 hours).
2. Using a small aluminum weighing boat and a six-place analytical balance, weigh out 0.1 to 1 mg of the sample. The amount weighed out should contain a quantity of quartz which will produce an absorbance which is measurable, but which is not greater than about 0.9.

NOTE: The weighed amount of sample and the amount of KBr (step 3) are specified for the Wilks Mini-press, which produces pellets approximately 8 mm in diameter. Adjust the amounts appropriately if another pellet press is used.

3. Quantitatively transfer the weighed sample to a small mortar and grind it thoroughly. Add between 75 and 100 mg dry KBr and mix it thoroughly with the ground sample.
4. Quantitatively transfer the mixture to the pellet press. Press the pellet according to the manufacturer's instructions.

NOTE: Weighing paper and a camel's hair brush are helpful in making the transfer.

5. Scan the pellet from 1000 cm^{-1} to 600 cm^{-1} , using a blank KBr pellet as background. Rotate the pellet 90 degrees and obtain another spectrum. Measure and record the mean peak absorbance at 798 cm^{-1} for the sample.
6. Calibration and Quality Control.
 - a. Prepare calibration standards, using dry Min-U-Sil 30, in exactly the same manner as samples (steps 2-5) and plot peak absorbance vs. micrograms SiO_2 .
 - b. Analyze bulk sample of known quartz content and prepare a control chart of recovery for use with subsequent analyses.