

SILICA, AMORPHOUS

7501

SiO₂

MW: 60.08

CAS: Table 1

RTECS: Table 1

METHOD: 7501, Issue 3		EVALUATION: PARTIAL		Issue 1: 15 May 1985 Issue 3: 15 March 2003	
OSHA:	Table 1	PROPERTIES:		solid; d 2.2 g/mL; MP >1600 °C	
NIOSH:	Table 1				
ACGIH:	Table 1				
SYNONYMS: fumed amorphous silica (Aerosil, silica aerogel, silicic anhydride); fused amorphous silica (Cab-o-sil, colloidal silica, xerogel, diatomaceous earth); hydrated amorphous silica (Hi-sil).					
SAMPLING			MEASUREMENT		
SAMPLER:	FILTER (Total) or CYCLONE + FILTER (Respirable) (10-mm cyclone, nylon or Higgins-Dewell + 5-µm PVC membrane)		TECHNIQUE:	X-RAY POWDER DIFFRACTION	
FLOW RATE:	Total: 1 to 3 L/min Nylon cyclone: 1.7 L/min HD cyclone: 2.2 L/min		ANALYTE:	Cristobalite	
VOL-MIN:	50 L		ASH:	Low temperature plasma; acid wash; deposit on PVC filter	
-MAX:	400 L @ 5 mg/m ³ (limit to ≤ 2 mg dust on filter).		XRD ANALYSIS:	XRD for quartz, cristobalite and tridymite before and after heating	
SHIPMENT:	Routine		HEAT:	1500 °C, 2 h (fumed amorphous silica) or 1100 °C, 6 h (other amorphous silica); redeposit on Ag filter	
SAMPLE STABILITY:	Stable indefinitely		CALIBRATION:	Standard suspensions of amorphous silica in 2-propanol, converted to cristobalite as for samples	
BLANKS:	2 to 10 field blanks per set		RANGE:	0.2 to 2 mg per sample	
BULK SAMPLE:	High volume area air sample required		ESTIMATED LOD:	0.005 mg per sample	
ACCURACY			PRECISION (S_r):	0.10 @ 0.4 to 5 mg; 0.33 @ 0.2 mg [1]	
RANGE STUDIED:	Not studied				
BIAS:	Not determined				
OVERALL PRECISION (S_{r,t}):	Not determined				
ACCURACY:	Not determined				
APPLICABILITY: This method is specific for amorphous silica in crystalline (e.g., quartz) matrices in the range 1 to 10 mg/m ³ for a 200-L air sample. Amorphous silica usually contains some crystalline silica [2]. See also discussion of crystalline silica in Chapter R of this volume [3].					
INTERFERENCES: Albite, ammonium phosphate and tridymite interfere with the largest peak of cristobalite. Quartz and cristobalite are quantitated prior to heat treatment and subtracted from the final quantity of cristobalite. Alkali and alkaline earth oxide prevent 100% conversion; these are removed by acid-wash prior to heat treatment. XRD signal intensity is proportional to particle size; similar particle size of samples and standards is desirable.					
OTHER METHODS: This method makes improvements in sample handling and quality assurance to P&CAM 316, which it replaces [4,5]. The XRD analysis steps are similar to those in Method 7500 (Silica, crystalline).					

REAGENTS:

1. Amorphous silica standard appropriate to the air sample, i.e., one of the following:
 - a. fumed amorphous silica, grade CAB-O-SIL® M-5, available from Cabot Corp.; www.cabot-corp.com;
 - b. gelled amorphous silica, grade Britesorb® D300 xerogel, available from The PQ Corp., PO Box 840, Valley Forge, PA 19482-0840; www.pqcorp.com;
 - c. diatomaceous earth amorphous silica, grade Celite 521, available from Fisher Scientific; www.fishersci.com;
 - d. precipitated amorphous silica, grade Zeothix® 265, available from J.M. Huber Corp.; www.hubermaterials.com.

NOTE 1: Some gelled or precipitated amorphous silicas contain up to 7% moisture. Dry all amorphous samples overnight at 115 °C [5].

NOTE 2: XRD signal intensity is proportional to particle size. Sieve the standards (10- μ m sieve), if necessary, to match the particle size expected in the samples

2. 2-Propanol, reagent grade.
3. Water, deionized.
4. Sodium chloride, reagent grade.
5. Hydrochloric acid, 2% (v/v). Dilute 20 mL conc. HCl to 1L with deionized water.
6. Desiccant.

* See SPECIAL PRECAUTIONS

EQUIPMENT:

1. Sampler:
 - a. Total dust: 37-mm diameter, 5.0- μ m pore size, polyvinyl chloride filter (MSA, Gelman GLA-5000, or equivalent) supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
NOTE: Gelman VM-1 and Millipore BS filters are unacceptable because of high ash or amorphous silica content.
 - b. Respirable dust: PVC filter (1.a. above) plus cyclone, 10-mm nylon or Higgins-Dewell (HD), with sampling head holder. Holder must keep the cassette, cyclone and coupler together rigidly so that air enters only at the cyclone inlet.
 - c. Area sample: PVC filter (1.a. above) at 3 L/min.
2. Personal sampling pumps 1 to 3 L/min (total or area); 1.7 L/min (nylon cyclone) or 2.2 L/min (HD cyclone).
3. Filters, PVC, 25-mm diameter, 0.45- μ m pore size.
4. Filters, silver membrane, 25-mm diameter, 0.45- μ m pore size, available from Sterlitech Corp., 22027 70th Ave S, Kent, WA 98032-1911; www.sterlitech.com.
5. X-ray powder diffractometer with copper target X-ray tube and scintillation detector.
6. Glue or tape for securing Ag filters to XRD holders.
7. Reference specimen (mica, Arkansas stone or other stable standard) for data normalization.
8. Low temperature plasma asher (LTA) or muffle furnace.
9. Filtration apparatus with side-arm vacuum flask and 25- and 37-mm filter holders.
10. Sieve, 10- μ m pore size, for wet sieving.
11. Furnace capable of maintaining 1100 °C for 6 h or 1500 °C for 2 h and of temperature programming to 500 °C at 50 °C/min.
12. Crucibles, platinum, with covers.
13. Analytical balance (0.01 mg).
14. Stirrer, magnetic, with thermally-insulated top.
15. Ultrasonic bath or probe.
16. Pipets, 2-to 25-mL.

EQUIPMENT - cont.:

17. Volumetric flasks, 1-L.
18. Desiccator.
19. Bottle, 1-L, with ground glass stopper.
20. Drying oven.
21. Wash bottle, polyethylene.
22. Mortar and pestle, agate.
23. Rubber policeman.
24. Beakers, 100-mL, with watchglass covers.

SPECIAL PRECAUTIONS: 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. Sample at 1 to 3 L/min (total and area), 1.7 L/min (nylon cyclone) or 2.2 L/min (HD) for a total sample size of 50 to 400 L.

NOTE 1: Do not allow the cyclone to be inverted at any time. Turning the cyclone to anything other than a horizontal orientation may deposit over-sized 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 to be 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 [6]. 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:

3. Ash the sample filter in a 100-mL beaker in the LTA according to manufacturer's instructions. After ashing, carefully (so as to avoid loss of sample) add 50 mL 2% HCl to each beaker.
4. Cover the beaker with a watchglass. Agitate in an ultrasonic bath for at least 3 min (until the agglomerated particles are broken up). Wash the underside of the watchglass with distilled water, collecting the washings in the same beaker.
5. Place a 25-mm PVC filter in the filtration apparatus. Attach the funnel securely over the entire filter circumference. With no vacuum, pour 2 to 3 mL deionized water onto the filter. Pour the sample suspension from the beaker into the funnel, and apply vacuum. After the transfer, rinse the beaker several times with deionized water and add rinsings to funnel for a total volume of 20 mL. Allow the suspension to settle for a few minutes prior to filtration. Do not wash the chimney walls or add deionized water to the chimney after filtration has begun. Rinsing the chimney can disturb the thin layer deposition. When filtration is complete, keep vacuum on until filter is dry. Remove the filter with forceps and attach it to the sample holder for XRD analysis.

CALIBRATION AND QUALITY CONTROL:

6. Weigh ca. 100 mg dried amorphous silica to the nearest 0.01 mg. Quantitatively transfer to a 1-L bottle using 1.00 L 2-propanol. The resulting concentration is 100 µg/mL.
7. Suspend the powder in 2-propanol using an ultrasonic probe or bath for 20 min. Immediately move the 1-L bottle to a magnetic stirrer with thermally-insulated top and add a stirring bar to the suspension. Allow the solution to return to room temperature before withdrawing aliquots.
8. Prepare a series of standard filters, in triplicate, over the range 0.005 to 2 mg per sample.
 - a. Mount a 37-mm PVC filter on the filtration apparatus. Place several mL 2-propanol on the filter. Turn off the stirrer and shake the bottle vigorously by hand. Immediately remove the stopper and withdraw an aliquot (e.g., 2 to 25 mL) by pipet from the center at half-height of the suspension. Do not adjust the volume in the pipet by expelling part of the suspension. If more than the desired aliquot is withdrawn, discard the aliquot in a beaker, rinse and dry the pipet, and take a new aliquot. Transfer the aliquot from the pipet to the filter, keeping the tip of the pipet near the surface but not submerged in the delivered suspension.
 - b. Rinse the pipet with several mL 2-propanol, draining the rinse into the funnel. Repeat the rinse several more times.
 - c. Allow the suspension to settle for a few minutes prior to applying vacuum. Apply vacuum and rapidly filter the suspension. Do not wash down the sides of the funnel after the deposition is in place since this will rearrange the material on the filter. Leave vacuum on until the filter is dry. When thoroughly dry, mount the filter in the XRD sample holder.
9. Prepare and analyze standard filters exactly like samples.
 - a. Ash in LTA; redeposit on 25-mm PVC filters (steps 3 through 5).
 - b. Analyze by XRD (step 13).
 - c. Heat to convert amorphous silica to cristobalite; redeposit on Ag filters (steps 14 through 16).
 - d. Analyze by XRD (step 17).
10. Prepare calibration graph (I_x° vs. µg of standard).

NOTE: Poor repeatability (i.e., $S_r > 0.1$) at any given level indicates that new standards should be made. The data should lie along a straight line. A weighted least squares ($1/S^2$ weighing) is preferable. Curvature can be eliminated with absorption corrections (step 20) [7].
11. Select six silver membrane filters to be analyzed as media blanks. Make the selection randomly from the same box of filters used for redepositing samples. Mount each media blank on the filtration apparatus and apply vacuum to draw 5 to 10 mL of 2-propanol through the filter. Remove, let dry and mount on XRD holders. Determine net normalized intensity for the silver peak, \hat{I}_{Ag} , for each media blank. Obtain an average value for the six media blanks, \hat{I}_{Ag}° .

NOTE: The analyst is a critical part of this analytical procedure [3]. A high level of analyst expertise is required in order to optimize instrument parameters and correct for matrix interferences either during the sample preparation phase or the data analysis and interpretation phase. XRD analysts should have some training (university or short course) in mineralogy or crystallography in order to have a background in crystal structure, diffraction patterns and mineral transformation. In addition, an intensive short course in the fundamentals of X-ray diffraction can be useful.

MEASUREMENT:

12. Obtain a qualitative X-ray diffraction scan (e.g., 10 to 80 °2θ) of the bulk (high-volume respirable) sample to determine the presence of free silica polymorphs and interferences. The diffraction peaks are:

<u>Mineral</u>	<u>Peak (2-Theta Degrees)</u>		
	<u>Primary</u>	<u>Secondary</u>	<u>Tertiary</u>
Quartz	26.66	20.85	50.16
Cristobalite	21.93	36.11	31.46
Tridymite	21.62	20.50	23.28
Silver	38.12	44.28	77.47

NOTE: For quantitative determination of amorphous silica in bulk samples, wet-sieve a portion of the bulk sample through a 10- μm sieve with 2-propanol in an ultrasonic bath. Evaporate the alcohol and dry in an oven 2 h. Weigh out, in triplicate, 2-mg portions of the sieved dust and transfer to beakers. Add 10 mL 2-propanol, deposit on a PVC filter (step 5) and continue with steps 13 through 17.

13. Perform the following for each sample, working standard and blank filter.
 - a. Mount the reference specimen. Determine the net intensity, I_r , of the reference specimen before and after each filter is scanned. Use a diffraction peak of high intensity that can be rapidly but reproducibly ($S_r < 0.01$) measured.
 - b. Mount the sample, working standard, or blank filter. Measure the diffraction peak area for each silica polymorph. Scan times must be long, e.g., 15 min (longer scan times will lower the limit of detection).
 - c. Measure the background on each side of the peak for one-half the time used for peak scanning. The sum of these two counts is the average background. Determine the position of the background for each sample.
 - d. Calculate the net intensity, I_x , (the difference between the peak integrated count and the total background count).
 - e. Calculate and record the normalized intensity, \hat{I}_x , for each peak:

$$\hat{I}_x = \frac{I_x}{I_r} \cdot N$$

NOTE: Select a convenient normalization scale factor, N, which is approximately equivalent to the net count for the reference specimen peak, and use this value of N for all analyses. Normalizing to the reference specimen intensity compensates for long-term drift in X-ray tube intensity. If intensity measurements are stable, the reference specimen may be run less frequently and the net intensities should be normalized to the most recently-measured reference intensity.

14. Remove the PVC filter from the XRD holder, fold the filter carefully and place it in a platinum crucible in the furnace. Raise the temperature of the furnace slowly (ca. 50 $^{\circ}\text{C}/\text{min}$) to 500 $^{\circ}\text{C}$ to ash the filter. When ashing is complete (ca. 0.5 h), raise the temperature to 1500 $^{\circ}\text{C}$ and maintain at 1500 $^{\circ}\text{C}$ for 2 h (for fumed amorphous silica) or to 1100 $^{\circ}\text{C}$ and maintain at 1100 $^{\circ}\text{C}$ for 6 h (for other amorphous silicas). Turn the furnace off and let the crucibles cool overnight in the furnace.
15. Place ca. 10 mg NaCl in the crucible and mix with the ash in the crucible. Transfer contents of the crucible to an agate mortar and grind to a fine powder using an agate pestle. Add distilled water from a polyethylene squeeze bottle to the mortar. Use a rubber policeman to stir. When the NaCl is dissolved, transfer the solution to a 100-mL beaker (hold the rubber policeman at the edge of the mortar to guide the flow into the beaker). Rinse mortar, pestle, crucible, and rubber policeman, collecting rinsings in the beaker. Cover the beaker with a watchglass and place in an ultrasonic bath for 2 to 3 min.

NOTE 1: Use extreme care to avoid air currents when working with the dry sample, as it is easily lost in the form of an aerosol.

NOTE 2: Use uniform grinding techniques to produce similar particle size in standards and samples.

16. Wash the underside of the watchglass and collect rinsings in the beaker. Place a silver membrane filter in the filtration apparatus and filter the contents of the beaker (step 5).
17. Mount the silver membrane filters in the XRD instrument and:
 - a. Analyze for the three silica polymorphs (step 13); and
 - b. Determine the normalized count, \hat{I}_{Ag} , of an interference-free silver peak on the sample filter following the same procedure. Use a short scan time for the silver peak (e.g., 5% of scan time for analyte peaks) throughout the method.

CALCULATIONS:

18. Calculate the concentration of amorphous silica, C (mg/m^3), as the difference in cristobalite concentrations measured before and after heat treatment in the air volume sampled, V (L):

$$C = \frac{\frac{\hat{I}'_x - b}{m} f(t) - \frac{\hat{I}_x - b}{m}}{V}, \text{mg} / \text{m}^3$$

- \hat{I}'_x = normalized intensity for cristobalite sample peak on the Ag filter (step 17.a)
 \hat{I}_x = normalized intensity for cristobalite sample peak on the PVC filter before heating (step 13)
 b = intercept of calibration graph (\hat{I}_x^o vs. μg)
 m = slope of calibration graph, counts/ μg
 $f(t)$ = $-\text{R} \ln T / (1 - T^{\text{R}})$ = absorption correction factor (Table 2)
 R = $\sin(\Theta_{\text{Ag}}) / \sin(\Theta_x)$
 T = $\hat{I}_{\text{Ag}} / (\text{average } \hat{I}_{\text{Ag}}^o) = \text{transmittance of sample}$
 \hat{I}_{Ag} = normalized silver peak intensity from sample (step 17.b)
 \hat{I}_{Ag}^o = normalized silver peak intensity from media blanks (average of six values)

NOTE: Compute the applicable OSHA standard using the formulae in Table 1 and the % crystalline silica found in the air sample before heat treatment.

EVALUATION OF METHOD:

This method is based on NIOSH P&CAM 316 [4,5] which was further evaluated with field samples in July, 1982 [1]. The relative standard deviation was determined to be related to the type of amorphous silica; gelled, fumed, and precipitated amorphous silica yielded 4.4%, 8.2%, and 4.7%, respectively, over the range of 0.5 to 5 mg. The method was further evaluated using 11 different types of gelled, precipitated, and fumed amorphous silicas and diatomaceous earth [8], with the following conclusions:

1. Not all fumed silicas converted to cristobalite at 1100 °C. A higher temperature (1500 °C) was needed to convert all the fumed silicas to cristobalite.
2. The moisture content of the gelled and precipitated silicas was ca. 7%; of diatomaceous earth, ca. 4%; and of fumed, from 0.5 to 3%.
3. The calibration curves from the four different types of amorphous silicas indicated very similar slopes ($S_r = \pm 6.6\%$).
4. Comparing the four slopes to a slope of a pure respirable cristobalite material, they were running approximately 30% lower in slope value. Therefore, field samples of amorphous silicas must be compared only to standards prepared from amorphous silicas.
5. Precision studies at 0.2-, 1-, and 2.5-mg levels (six samples per level) of gelled, precipitated, diatomaceous earth, and fumed silicas indicated a pooled precision, \bar{S}_r , of 8.8, 10.5, 5.6, and 21.5%, respectively, for the above silicas.
6. Recovery studies of the same silicas and concentration levels indicated average recoveries of 82, 115, 95, and 111%, respectively, with pooled \bar{S}_r equal to 18.2, 13.1, 12.9, and 15.3%, respectively, for the gelled, precipitated, and fumed silicas, and diatomaceous earth.

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METHOD REVISED BY:

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TABLE 1. CAS Numbers, RTECS Numbers, and Exposure Limits for Amorphous Silica Forms

Amorphous Forms	CAS#	RTECS	OSHA PEL (mg/m ³)	NIOSH PEL (mg/m ³)	ACGIH TLV (mg/m ³)
diatomaceous earth, <1% crystalline SiO ₂	61790-53-2	HL8600000	80% SiO ₂	6	10 (total)
precipitated, and gel	7699-41-4, 112926-00-8	VV8850000	80% SiO ₂	6	10 (total)
fumed	69012-64-2 112945-52-5	VV310000	80% SiO ₂	–	2 (respir)
fused	60676-86-0	VV7328000	–	–	0.1 (respir)

Table 2. MATRIX ABSORPTION CORRECTION FACTORS FOR CRISTOBALITE (HEAT-CONVERTED AMORPHOUS SILICA) AND SILVER PEAKS.

		Degrees 2- θ				
Cristobalite Silver	21.93	21.93		21.93	21.93	
	38.12	44.28		38.12	44.28	
	T	f(T)	f(T)	T	f(T)	f(T)
	1.00	1.0000	1.0000	0.74	1.2806	1.3278
	0.99	1.0087	1.0100	0.73	1.2944	1.3440
	0.98	1.0174	1.0201	0.72	1.3084	1.3605
	0.97	1.0264	1.0305	0.71	1.3226	1.3774
	0.96	1.0355	1.0410	0.70	1.3372	1.3946
	0.95	1.0447	1.0517	0.69	1.3521	1.4122
	0.94	1.0541	1.0625	0.68	1.3673	1.4303
	0.93	1.0636	1.0736	0.67	1.3829	1.4487
	0.92	1.0733	1.0849	0.66	1.3987	1.4675
	0.91	1.0831	1.0963	0.65	1.4150	1.4868
	0.90	1.0932	1.1080	0.64	1.4316	1.5064
	0.89	1.1034	1.1199	0.63	1.4485	1.5266
	0.88	1.1137	1.1320	0.62	1.4659	1.5472
	0.87	1.1243	1.1443	0.61	1.4836	1.5684
	0.86	1.1350	1.1568	0.60	1.5018	1.5900
	0.85	1.1460	1.1696	0.59	1.5204	1.6122
	0.84	1.1571	1.1827	0.58	1.5394	1.6349
	0.83	1.1685	1.1959	0.57	1.5590	1.6582
	0.82	1.1800	1.2095	0.56	1.5790	1.6820
	0.81	1.1918	1.2232	0.55	1.5995	1.7065
	0.80	1.2038	1.2373	0.54	1.6205	1.7317
	0.79	1.2160	1.2516	0.53	1.6421	1.7575
	0.78	1.2284	1.2663	0.52	1.6642	1.7840
	0.77	1.2411	1.2812	0.51	1.6870	1.8112
	0.76	1.2540	1.2964	0.50	1.7103	1.8391
	0.75	1.2672	1.3199			