

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 (NIST), Gaithersburg, MD 20899; www.nist.gov.
 - b. Tridymite* (210-75-0043), available from U.S. Geological Survey, Box 25046, MS 973, Denver, CO 80225.
2. Hydrofluoric acid, 48% (HF).*
3. Orthophosphoric acid, 85% H₃PO₄.*
4. Silica-free water. All water used must be deionized and stored in polyethylene containers.
5. Hydrochloric acid (HCl),* 1:10 v/v conc. HCl in deionized water.
6. Sulfuric acid, 10 N.* Cautiously add 555 mL conc. H₂SO₄ to about 1.3 L of deionized water. Cool. Dilute to 2 L.
7. Nitric acid, conc.*
8. Perchloric acid, conc*. Use only if samples have been collected on PVC filters.
9. Boric acid solution, 5%. 200 g boric acid crystals in 4 L warm deionized water. Cool. Filter with vacuum through a 0.45- μ m membrane filter. Store in a polyethylene container.
10. Molybdate reagent. Dissolve 50 g ammonium molybdate tetrahydrate in about 400 mL deionized water. Add 50 mL conc. sulfuric acid. Cool. Dilute to 500 mL. Store in dark.
11. Reducing solution. Dissolve 9 g sodium bisulfite in 80 mL deionized water. In 10 mL deionized water, dissolve 0.7 g anhydrous sodium sulfite and 0.15 g 1-amino-2-naphthol-4-sulfonic acid, in that order. Combine these solutions and dilute to 100 mL with deionized water. Stable about one month if stored in refrigerator.
12. Silica stock standard, 0.5 mg/mL. Dissolve 250 mg quartz in 10 mL 48% HF. Dilute to 500 mL with silica-free water. Store in a polyethylene container. Stable indefinitely.

* See SPECIAL PRECAUTIONS.

EQUIPMENT:

1. Sampler:
 - a. Filter: Mixed cellulose ester (MCE) filter, 37-mm, 0.8- μ m, or polyvinyl chloride (PVC) filter, 37-mm, 5.0- μ m pore size, supported with backup pad in a two-piece, 37-mm cassette filter holder (preferably, conductive) held together by tape or cellulose shrink band.
NOTE: If PVC filters are used, a perchloric acid fume hood, low-temperature radio-frequency plasma asher or muffle furnace will be needed to ash them (Appendix B).
 - 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 a two-piece filter cassette. Sample closed face at 3 L/min.
3. Sampling pumps: HD cyclone, 2.2 L/min; nylon cyclone, 1.7 L/min; and area sampler, 3 L/min.
4. Precision heater, 550-watt, 115-V, Type RH; 750-watt variable transformer with built-in voltmeter; variable speed clinical rotator, about 30 to 80 rpm range (can be achieved with a variable transformer).
5. Stopwatch or laboratory timer.
6. Phillips beakers, borosilicate glass, 250-mL; short-stemmed glass funnels with bent stems (must be done by laboratory); crucible tongs with tygon or rubber-padded tips; polyethylene stirring rods; polyethylene 50-mm discs.
7. Vacuum filtration assembly: MCE membrane filters, 0.45- μ m pore size, 47-mm diameter; filter funnel, including membrane mount and flask assembly, 47-mm.
8. Buret, polypropylene, 10-mL; polyethylene reagent bottles for water, boric acid, and standard solutions.
9. Constant temperature bath, 40 °C.
10. Spectrophotometer, at 420 to 820 nm and 1-cm cuvettes.
11. Hotplate, 150 °C surface temperature.
12. Graduated cylinder or graduated pipet, 10- and 25-mL.
13. Polyethylene graduated cylinder or pipets, 25- and 5-mL.

SPECIAL PRECAUTIONS: Avoid inhaling silica dust [5]. Use personal protective equipment to prevent contact of acids with the skin. HF dissolves glass. Use plastic labware for all solutions containing HF. Concentrated acids are corrosive.

SAMPLING:

1. Calibrate each personal sampling pump with a representative sampler in line.
2. Sample at $2.2 \pm 5\%$ L/min with HD cyclone and $1.7 \pm 5\%$ L/min with nylon cyclone for a total sample size of 400 to 800 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 [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 [5,7]

SAMPLE PREPARATION:

NOTE: Successful use of this method depends on close attention to details and uniformity in sample handling procedures.

3. Place a weighed sample containing no more than 2.5 mg SiO_2 , or a membrane filter sample, in a 250-mL Phillips beaker. Add 3 to 4 mL conc. HNO_3 to ash membrane filters. Heat on a hotplate to absence of brown fumes.
4. Add an additional 2 mL conc. HNO_3 and heat to dryness. Repeat this step until any remaining residue is white.

NOTE: Ash PVC filters using 2 mL conc. HClO_4 . Heat slowly until the filter shrinks, turns brown and is dissolved. Add additional portions of HClO_4 if necessary. If a perchloric acid hood is not available, see APPENDIX B for alternate ashing procedures for PVC filters. Pretreatment procedures to remove various contaminants from bulk samples are outlined in reference [7].

5. Add 25 mL 85% H_3PO_4 to the beaker. Cover the beaker with a bent-stem funnel. Make sure that the tip of the funnel stem touches the wall of the flask. Start reagent blanks at this time.

NOTE: The bent-stem funnel is used to prevent too rapid dehydration of the sample and to prevent spattering.

6. Place the 550-watt heater on the rotator in a fume hood. Preheat the heater and adjust to maintain a temperature of 240°C. Heat each sample and blank for exactly 8 min, swirling it by the action of the variable speed rotator.

NOTE: The solution in the flask should reach 240°C during this procedure.

7. Remove the beaker from the heater with padded tongs and swirl it for 1 min. Allow the beaker to cool. Add about 125 mL warm (60 to 70°C) deionized water and swirl to mix completely.
8. Filter the sample with suction through a 47-mm filter. Wash thoroughly with 1:10 HCl.
9. Place the 47-mm filter in the bottom of a 150-mL polyethylene beaker. Add 0.5 mL 48% HF to the filter surface. Float a thin polyethylene disc of about 50-mm diameter over the 47-mm filter and cover the beaker. Allow to stand for 30 min.

CALIBRATION AND QUALITY CONTROL:

10. Prepare a calibration graph for the silico-molybdate range.
 - a. Dilute 1-, 2-, 3-, 4-, 5- and 6-mL aliquots of the silica stock standard (NIST SRM 1878a quartz) to 25 mL with silica-free water in polyethylene beakers.
 - b. Analyze together with samples and blanks (steps 14 through 16).
 - c. Plot absorbance vs. mg SiO₂.
11. Prepare a calibration graph in the molybdenum blue range.
 - a. Dilute the working standards in step 10 1:25.
 - b. Analyze the resulting standard solutions (steps 14 through 16).
 - c. Plot absorbance vs. mg SiO₂.
12. Prepare control samples containing a silicate compound (about 50 mg MgSiO₄ sample) in addition to the quartz. Recovery of quartz is low and precision is much worse if quartz only is present during the phosphoric acid treatment.

NOTE 1: Calibration standards are limited to specified 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. None have been found to be acceptable alternatives to the certified standards cited within this method [3]. Standard reference materials should be corrected for phase purity.

NOTE 2: Crystalline silica methods require standards of known purity, specific particle size distribution, and sample-to-sample homogeneity. Establishing traceability of secondary 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 within the industrial hygiene field. 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: Some training (university or short course) in geology or mineralogy of the analyst or laboratory management is useful to provide a background in crystal structure and mineral transformation in order to answer the questions that laboratory clients may have and to understand any matrix effects.

MEASUREMENT:

13. Add 25 mL silica-free water to samples in polyethylene beakers.
14. Add 50 mL boric acid solution. Stir well. Cover. Heat the solution in a 40 °C waterbath for 10 min.
15. Add 4 mL molybdate reagent while stirring, staggering the addition at 2-min intervals between samples. Exactly 20 min after the addition of the molybdate reagent, add 20 mL 10 N H₂SO₄ and stir thoroughly.
16. Note the color of the solution.
 - b. If a colorless solution results, allow it to stand for 2 to 5 min and add 1 mL 1-amino-2-naphthol-4-sulfonic acid reagent. Mix and read after 20 min at 820 nm against deionized water. This color is stable for several hours.
 - c. Record the absorbances of the sample, A, and reagent blank, B.

CALCULATIONS:

17. Calculate the concentration of crystalline silica, C (mg/m³), in the air volume sampled, V (L), using the slope, m (µg⁻¹) of the appropriate calibration graph:

$$C = \frac{(A - B)}{m \cdot V}$$

EVALUATION OF METHOD:

This method is based on the well-characterized Talvitie method [1,8,9,10].

REFERENCES:

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APPENDIX A:

INTERFERENCES

Some silicates may be resistant to phosphoric acid digestion [8]. Any silicates not removed by the phosphoric acid treatment will give a positive interference. Amorphous silica, if not completely removed by phosphoric acid treatment, will give a positive interference. Phosphate ion complexes molybdic acid to produce a yellow phosphomolybdate color which is dissipated by lowering the pH of the solution with 10 N sulfuric acid. Excess ferric ion (more than 1 mg) will consume the reducing agent and inhibit the reduction of silicomolybdate to molybdenum blue. If more than 1 mg ferric ion is present, it should be removed by pretreatment with 10:1 HCl:HNO₃.

APPENDIX B:

ALTERNATE ASHING PROCEDURES FOR PVC FILTERS

If a perchloric acid fume hood is unavailable, ash PVC filters with one of the following methods.

1. **Muffle furnace ashing:** Wash the filters with 25% v/v HCl if the samples contain a significant amount of calcite (20% of the total dust loading); otherwise, proceed to next paragraph. Place a 0.5- μ m, 47-mm PVC filter in the filtration apparatus. Center the sample filter on top of the first filter. Clamp the filter funnel over the frit so that the dust deposit is completely exposed. Add 10 mL HCl solution and 5 mL 2-propanol to the filter funnel; allow to stand for 5 min. Apply vacuum to aspirate the acid/alcohol solution from the filter. Wash with three 10-mL portions of deionized water. Release the vacuum.

Place the filter samples in porcelain crucibles, cover loosely and ash in a muffle furnace for 2 h at 600 °C (800 °C if graphite is present). Add several mL of 2-propanol to the ash, scrape the crucible to loosen all particles and transfer the residue to a 250-mL borosilicate glass Phillips beaker. Wash crucible several times and add wash to the beaker. Heat on a sparkless hotplate to evaporate the 2-propanol. When beaker is dry, proceed with step 4 of sample preparation.

2. **Low temperature ashing:** Place the filters in 50-mL glass beakers within the LTA so that the sample exposure to the plasma is optimized. Ash according to manufacturer's instructions. After ashing, add 2-propanol to the beaker to transfer the residue to a 250-mL borosilicate Phillips beaker. Wash the beaker with 2-propanol several times, adding the washings to the Phillips beaker. Heat on a sparkless hotplate to remove the 2-propanol. When the beaker is dry, proceed to step 4 of sample preparation.