

Release of Crystalline Silica Nanoparticles During Engineered Stone Fabrication

Introductory Information

Inhalation exposure to respirable crystalline silica (RCS) during fabrication of engineered stone-based kitchen countertops has been on the rise in recent years and has become a significant occupational health problem in the United States and globally. Little is known about the presence of nano-crystalline silica (NCS), i.e., particles below 100 nm. We present a methodology to quantify the crystalline silica content in the sub-100 nm size fraction of the aerosol released during engineered stone fabrication using X-ray diffraction (XRD) and Fourier transform Infrared (FT-IR) spectroscopy. Aerosol was generated in test chamber designed per EN 1093-3 and sampled using cascade impactors. XRD and FT-IR analysis showed the presence of both α -quartz (15 – 60 %) and cristobalite (10 – 50 %) polymorphs in all size fractions. With increasing particle size, the cristobalite content increased. 70 % of the total aerosol mass in the sub-100 nm fraction was found to be crystalline silica, qualitatively confirmed by electron diffraction and electron energy loss spectroscopy. Presence of other minerals was detected in all size fractions; no polymeric resin binder was detected in the sub-100 nm fraction. Although, the sub-100 nm fraction was about 1 % of the aerosol mass, it accounted for 4 – 24 % of the aerosol surface area based on total lung deposition. If the surface area is a more relevant exposure metric, the assessment of efficacy of current engineering control systems using mass as an exposure metric may not provide adequate protection.

Experimental Methods

Experiments were designed to collect aerosol from grinding a commercially available engineered stone inside a test chamber designed per the European Standard EN 1093-3. The aerosol was carried downstream to a measurement duct at a controlled and constant airflow velocity of about 2.26 m/s corresponding to a flow velocity of 0.11 m/s in the chamber. The measurement duct contained near-isokinetic sampling probes for sampling and monitoring the aerosol.

Sample collection

- Aerosol generated by manually grinding a stack of the engineered stone using a hand-held pneumatic angle grinder (GPW-216, Gison Machinery Co., Ltd., Taiwan) with coarse, diamond grinding cup wheel (Model SIS-4SPCW-SC, Stone Industrial Supplies, Inc., USA).
- Each test comprised of 12 minutes of active grinding time and 3 minutes idling time. Aerosol collected 6 times.
- Aerosol sampled using aerodynamic particle sizer (Model 3321, TSI Inc.) and Micro-Orifice, Uniform-Deposit Impactor (MOUDI) (Model 110-R, TSI Inc.) through near-isokinetic sampling ports.
- For four replicate tests, aerosol collected on pre-weighed PVC filters (47 mm, 5 μ m pore size, SKC, Inc.) loaded onto the MOUDI impactor substrates.
- For other two replicate tests, aerosol collected on pre-weighed aluminum foil (47 mm, TSI Inc.), and directly on the MOUDI substrates.
- Impactor nozzles cleaned using 2-propanol after each test. MOUDI's air flow rate calibrated through a mass flow meter (Model 4043H, TSI Inc.) before each use. The pressure drops in the MOUDI remained consistent before and during measurements.

Calibration samples

- In XRD and FT-IR methods, SRM 1878a (NIST), SRM 1878b (NIST), and Min-U-Sil 5 (US Silica Company, Berkeley Springs, WV) were used for α -quartz calibration, whereas SRM 1879b (NIST) was used for cristobalite calibration.
- For XRD calibration studies on α -quartz, size fractionated SRM 1878a, and Min-U-Sil 5 samples were obtained using Quartz Crystal Microbalance MOUDI (QCM MOUDI, TSI Inc.), and MOUDI impactors, respectively. SRM 1878a was nebulized from an aqueous suspension while Min-U-Sil 5 was aerosolized by vortex shaking. The collected particles were suspended in 2-propanol (A461-

212, Optima LC/MS Grade, Fisher Scientific) and redeposited on pre-weighed silver filters (25 mm, pore size 0.45 μm , SKC, Inc.).

- For XRD calibration studies on cristobalite, size fractionated SRM 1879b samples were obtained using MOUDI impactor. SRM 1879b was aerosolized by vortex shaking and the collected particles were suspended in 2-propanol (A461-212, Optima LC/MS Grade, Fisher Scientific) and redeposited on pre-weighed silver filters (25 mm, pore size 0.45 μm , SKC, Inc.).
- For FT-IR calibration studies on α -quartz, size fractionated SRM 1878b, and Min-U-Sil 5 samples were obtained using MOUDI impactor. Both reference materials were aerosolized by vortex shaking. While Min-U-Sil 5 was collected directly on PVC filters (47 mm, 5 μm pore size, SKC, Inc.) loaded onto the MOUDI impactor substrates, the collected SRM 1878b particles were suspended in 2-propanol (A461-212, Optima LC/MS Grade, Fisher Scientific) and redeposited on pre-weighed PVC filters (25 mm, pore size 5 μm , SKC Inc.).
- For FT-IR calibration studies cristobalite, size fractionated SRM 1879b (aerosolized by vortex shaking) samples were obtained using MOUDI impactor. One replicate sample was collected directly on PVC filters (47 mm, 5 μm pore size, SKC, Inc.) loaded onto the MOUDI impactor substrates, while two other replicates were suspended in 2-propanol (A461-212, Optima LC/MS Grade, Fisher Scientific) and redeposited on pre-weighed PVC filters (25 mm, pore size 5 μm , SKC Inc.).
- For FT-IR calibration studies on α -quartz, additional size-fractionated Min-U-Sil 5 samples with aerodynamic diameters of 0.32 μm , 0.56 μm , and 1 μm were collected independently using the Aerodynamic Aerosol Classifier (AAC; Cambustion Ltd, Cambridge, United Kingdom) and NanoSpot Collector (Aerosol Devices Inc., Fort Collins, CO).
- For conventional XRD calibration studies on α -quartz, and cristobalite, stock suspensions of 100 $\mu\text{g/ml}$ for SRM 1878b (used as is), and SRM 1879b (used as is) in 2-propanol (A461-212, Optima LC/MS Grade, Fisher Scientific) were prepared. Aliquots of the stock suspension were vacuum

filtered through pre-weighed silver filters (25 mm, pore size 0.45 μm , SKC, Inc.) to obtain samples with mass loadings of approximately 12 μg , 60 μg , 230 μg , and 470 μg for both reference materials.

- For conventional FT-IR calibration studies on α -quartz, and cristobalite, HPS standards (ISO 17034 Certified and NIST-traceable) with mass loadings ranging from 10 μg to 500 μg for SRM 1878b, and 5 μg to 250 μg for SRM 1879b, respectively, on 25 mm PVC filters were used as is.
- All filters were conditioned in the humidity controlling chamber.
- All gravimetric measurements were performed on an ultra-micro balance (Model XPR6U, Mettler-Toledo). Each filter was pre- and post-weighed thrice and the difference of the averages was the representative mass of the aerosol/calibration material.

Sample Analysis Methods

Different analytical methods were used to determine the crystalline silica content in different size-fractions of the grinding aerosol from the engineered stone.

X-Ray Diffraction (XRD) Measurements

- The grinding aerosol collections on aluminum foil substrates from the MOUDI were resuspended in 2-propanol (A461-212, Optima LC/MS Grade, Fisher Scientific). Resuspensions were vacuum filtered on pre-weighed silver filters (25 mm, 0.45 μm pore, SKC, Inc.).
- Silver filters were mounted onto holders atop a “zero background” backing plate made of silicon single crystal.
- The crystalline silica contents in the size-fractionated aerosol samples were measured using an X-ray diffractometer (Empyrean series 2, PANalytical, The Netherlands). The diffractometer was equipped with a 1.8 kW long fine focus Cu X-ray tube operated at 45 kV and 40 mV, 0.04 rad Soller slit, 10mm mask, 2° anti-scatter slit and 1/2° divergence slit, Bragg-Brentano HD, and PIXcel 3D detector. XRD measurements were conducted over a 2 θ -range from 20° to 40° with 0.02° step size for each sample.

- During XRD batch measurements, an instrument reference standard (PANalytical, The Netherlands) was analyzed to account for the long-term tube drift. The peak intensity of this standard was used as a correction factor following the NIOSH 7500 method.
- The calibration curves for quartz and cristobalite were obtained by plotting the net height of each primary peak (located at $26.69^\circ 2\theta$ and $22.02^\circ 2\theta$ for quartz and cristobalite, respectively) as a function of the reference material mass on the filter for each size-fractionated sample.
- The size-fractionated calibration curves were obtained by plotting the slopes from these calibration curves as a function of size.
- The conventional calibration curves were obtained by plotting the net height of each primary peak (located at $26.69^\circ 2\theta$ and $22.02^\circ 2\theta$ for quartz and cristobalite, respectively) as a function of the reference material mass on the filter.

Fourier transform Infrared (FT-IR) spectroscopy Measurements

- The grinding aerosol collections on PVC filters from the MOUDI were used for FT-IR measurements.
- FT-IR absorbance was measured using an FT-IR spectrometer (Alpha-II, universal sample model, Bruker) with a spectral range of $400 - 4000 \text{ cm}^{-1}$ at 2 cm^{-1} resolution. For each sample, the absorption spectrum (averaged over 16 scans) was obtained three times.
- The calibration curves for quartz, and cristobalite, were obtained by plotting the net height of the absorbance band at 695 cm^{-1} (baseline between 680 cm^{-1} and 710 cm^{-1}), and 625 cm^{-1} (baseline between 610 cm^{-1} and 630 cm^{-1}), respectively, as a function of the reference material mass on the filter for each size-fractionated sample.
- The size-fractionated calibration curves were obtained by plotting the slopes from these calibration curves as a function of size.

- The conventional calibration curves were obtained by plotting the net height of absorbance bands (at 695 cm^{-1} , and 625 cm^{-1} or quartz, and cristobalite, respectively) as a function of the reference material mass on the filter.

Electron Microscopy

- Grinding aerosol collected directly on the MOUDI impactor substrates was transferred onto SEM pin stub mounts (Aluminum, grooved edge, Ted Pella, Inc.) with carbon conductive tabs (PELCO Image Tabs™, Ted Pella, Inc.), and TEM grids (400 mesh carbon coated Ni or Cu, SPI).
- For multi-particle analysis, a Phenom XL (Thermo Fisher Scientific, Waltham, MA, USA) scanning electron microscope (SEM) operated in the low-pressure mode ($\sim 1\text{ Pa}$) at 15 kV acceleration voltage and 1.7 nA probe current with a backscattered electron (BSE) detector and an energy dispersion spectrometer was used.
- To characterize individual particles at high magnifications, we used a JEOL 2100F (JEOL USA, Peabody, MA) scanning transmission electron microscope (STEM) with a field emission gun, equipped with an EDS detector (X-Max80T, Oxford Instruments America, Concord, MA) and a post-column Gatan Image Filter (GIF) (Tridiem 863, Gatan, Pleasanton, CA).
- Composition, crystallinity, and local electronic structure of individual silica particles in the samples were examined by energy-dispersive X-ray spectroscopy (EDS), selected area electron diffraction (SAED), and electron energy loss near edge structure (ELNES), respectively.

Raman spectroscopy Measurements

- The engineered stone surface was gently sanded with a 600-grit silicon carbide sandpaper (3M™ Wetordry™ Abrasive Sheet 413Q, 3M, Maplewood, MN).
- The sanded powder was suspended in 2-propanol (A461-212, Optima LC/MS Grade, Fisher Scientific) and vacuum filtered on a silver filter ($0.45\text{ }\mu\text{m}$ pore, SKC, Inc.).

- The crystalline silica polymorphs in the bulk powder from the engineered stone were determined using confocal-Raman spectroscopy (XploRA Plus, HORIBA France SAS, France) and X-ray diffraction.
- The Raman intensity was measured using a confocal-Raman microscope that is equipped with a confocal pinhole, a 785 nm laser source, a 100X/0.90 ∞ /0/FN22 objective (MPlan N, Olympus) and a CCD detector. The spectra were acquired in the wavenumber range of 50 – 550 cm^{-1} of Raman shift with a resolution of 1.8 cm^{-1} .

Optical Photothermal Infrared (O-PTIR) spectroscopy

- An advanced optical photothermal infrared (O-PTIR) spectroscopy microscope (Photothermal Spectroscopy Corp., Santa Barbara, CA) was used to detect the presence of polymeric resin in the sub-100 nm and respirable size fractions of the aerosol. Measurements were made on the same silver filters as used for XRD.
- The O-PTIR microscope is equipped with a tuneable mid-IR quantum-cascade laser (QCL) source (Block Engineering, Southborough, MA) and a 532 nm laser, both collimated through an 40X/0.78N.A. reflective objective (PIKE Technologies, Inc., Madison, WI).
- O-PTIR spectra were acquired in the wavenumber range of 771 – 1881 cm^{-1} with a resolution of 2 cm^{-1} .
- Hyperspectral images (5 μm x 2.7 μm) of aerosol deposited on silver filters were used to generate the O-PTIR spectra. A total of 1350 spectra were recorded at increments of 0.1 μm along both co-planar axes on each hyperspectral image.

Citations- Publications based on the dataset.

Rishi, K., Ku, B.K., Qi, C., Thompson, D., Wang, C., Dozier, A., Vogiazzi, V., Zervaki, O., and Kulkarni, P. Release of Nano-crystalline Silica During Engineered Stone Fabrication. ACS Omega 2024, 9, 51, 50308–50317, DOI: <https://doi.org/10.1021/acsomega.4c06437>

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