Annals of Work Exposures and Health, 2022, Vol. 66, No. 9, 1210–1214
https://doi.org/10.1093/annweh/wxac063
Advance Access publication 6 September 2022
Short Communication

Short Communication

Caution on Using Tetrahydrofuran for Processing Crystalline Silica Samples From Engineered Stone for XRD Analysis

Chaolong Qi*, Drew Thompson and H. Amy Feng

Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health, Division of Field Studies and Engineering, 1090 Tusculum Ave, MS: R5, Cincinnati, OH 45226, USA

*Author to whom correspondence should be addressed. Tel: 001 513-841-4532; e-mail: hif1@cdc.gov

Submitted 2 May 2022; revised 7 July 2022; editorial decision 6 August 2022; revised version accepted 12 August 2022.

Abstract

We conducted laboratory experiments to investigate a suspected effect of tetrahydrofuran (THF) on quantifying crystalline silica in samples collected from working with engineered stone when THF is used to process samples prior to the X-ray diffraction (XRD) analysis. Two groups of samples from grinding either engineered stone or granite were simultaneously taken from a laboratory testing system, with one group of samples using THF for processing and another group using muffle furnace for ashing. For each stone type, we also tested four levels of respirable dust loading on the samples by varying the grinding time from 1 to 8 min. Statistical analysis of the experimental results on crystalline silica contents of the two groups of samples showed that the difference between the two methods was not significant ($P \geq 0.05$) for the granite at all four levels of respirable dust loading and for the engineered stone at the two levels of respirable dust loading greater than 0.5 mg. However, the crystalline silica content from using THF processing was significantly lower ($P = 0.001$) than that from using muffle furnace ashing for engineered stone when the respirable dust loading levels were less than 0.5 mg. For the engineered stone dust samples with grinding times of 1 and 2 min, the average respirable dust loading was about 0.19 and 0.34 mg, respectively; while the crystalline silica content from using THF processing was 30.9 and 21.5% lower than that from using muffle furnace ashing, respectively. Since most full-shift samples from field assessments in this industry are expected to have respirable dust loading less than 0.5 mg, muffle furnace or radio frequency plasma ashing should be specified as the preferred sample processing method instead of the THF processing method for quantification of crystalline silica when engineered stone is expected to present to avoid artificially reduced silica content values, which are likely caused by the reactions between THF and the resins in engineered stone.

Keywords: engineered stone; crystalline silica; tetrahydrofuran

Published by Oxford University Press on behalf of The British Occupational Hygiene Society 2022.

Downloaded from https://academic.oup.com/annweh/article/66/9/1210/6692700 by Centers for Disease Control user on 15 November 2022

What's Important About This Paper?

There is increasing interest in crystalline silica exposures associated with engineered stone, but analytical methods using tetrahydrofuran (THF) prior to X-ray diffraction analysis may lead to underestimation of silica content in dust samples. This study found that crystalline silica content from using THF processing can be significantly lower (more than 30%) than that from using muffle furnace ashing for respirable dust samples collected from grinding an engineered stone containing resins. Muffle furnace or radio frequency plasma ashing methods are recommended instead of THF for crystalline silica analyses when the engineered stone contains resins.

Introduction

Engineered stone has become increasingly popular among consumers in recent years and is one of the most popular countertop options. Some engineered stone products can contain greater than 90% crystalline silica by mass with various polymer resins making up the remainder. Unfortunately, a large amount of dust can be produced during stone countertop manufacturing, fabrication, and installation, leading to overexposures to respirable crystalline silica (RCS) among the workers (NIOSH, 2016; Qi *et al.*, 2017). In the USA, the Occupational Health and Safety Administration (OSHA) set the Permissible Exposure Limit (PEL) of 0.05 mg m^{-3} for RCS as an 8-h time weighted average exposure (CFR, 2016).

Multiple clusters of silicosis related to RCS overexposures from working with engineered stone have been reported in recent years globally (Pascual *et al.*, 2011; Kramer *et al.*, 2012; Pérez-Alonso *et al.*, 2014; Friedman *et al.*, 2015; Hoy *et al.*, 2018; Ronsmans *et al.*, 2018; Rose *et al.*, 2019). OSHA (OSHA, 2020) established a new National Emphasis Program in the USA, specifically targeting workers' RCS overexposure in the countertop industry. With the resulting anticipated increase in field assessments of workers' RCS exposure, it is critical to ensure the accuracy of the analytical method for crystalline silica. X-ray diffraction (XRD) is widely used to quantify crystalline silica collected on polyvinyl chloride (PVC) filters to assess RCS exposures. The standard National Institute for Occupational Safety and Health (NIOSH, 2003) Method 7500 in the US specifies three techniques to process the PVC filter after sample collection: muffle furnace ashing, radio frequency (RF) plasma ashing, or dissolution in tetrahydrofuran (THF). However, the OSHA Method ID-142 (2016), which was withdrawn since January 2020, only specifies the use of THF for sample preparation. Previous observation at NIOSH found that using THF to process samples containing polymer resins resulted in reactions between the resins and THF, which formed a paste-like residue on the redeposition apparatus, leading to artificially lower crystalline silica results. The plausible explanation is that the paste-like residue results in loss of silica particles during the redeposition process. It is not clear to us whether the residue may reduce the XRD signal from silica particles embedded inside even though they are redeposited. The presence of resins in engineered stone caused concern about the accuracy of RCS exposure measurements when THF is used to process the samples. This study aimed to demonstrate the effect THF posed on quantifying crystalline silica in samples from grinding a typical engineered stone.

Methods

Experimental design

We designed an experiment to compare RCS analyses using both muffle furnace ashing and THF dissolution as sample preparation methods for multiple samples simultaneously collected from grinding stone blocks in a laboratory testing system. We tested both a typical engineered stone product that contained 70–90% crystalline silica (as specified by its manufacturer) as well as a piece of granite. We hypothesized that there would be no significant difference between the two methods when RCS samples generated from granite, which does not contain resins, were analyzed, but significant differences might be observed between the two sample preparation methods when RCS samples from the engineered stone were analyzed. For each stone type, we conducted four sets of tests with different levels of respirable dust deposited on the samples, by varying the grinding times of 1, 2, 4, and 8 min, to examine whether dust loading could affect the method comparison.

Laboratory testing and sampling

We conducted the experiment in a testing system similar to the one described in earlier publications (Qi *et al.*, 2016; Kang *et al.*, 2019). Supplementary Fig. S1 is a diagram of the system and the sampling equipment. Different from the previous studies, a house ventilation system drove airflow through the test system by introducing particle-free air into the tool-testing

Downloaded from https://academic.oup.com/annweh/article/66/9/1210/6692700 by Centers for Disease Control user on 15 November 2022

chamber through a filter section that contained both pre- and HEPA filters. Stone blocks were mounted in the tool-testing chamber, which had two glove boxes on one side of the chamber which provided access for manually grinding the stone blocks using a handheld pneumatic grinder (GPW-216, Gison Machinery Co., Ltd., Taiwan) with a diamond grinding cup wheels (SIS-4SPCW-SC, Stone Industrial Supplies, Inc., Miami, FL, USA). The chamber connected to a 30-cm diameter duct, where representative air samples were taken. Multiple respirable dust samples were collected simultaneously from the dust cloud carried by the airflow through a sampling probe mounted on the duct (see Supplementary Fig. S1). More details on the operation of the system and sampling are in the Supplementary Information.

Analysis of crystalline silica

All the bulk and respirable dust samples were sent to a laboratory of Bureau Veritas North America (BVNA, Novi, MI, USA), which is accredited by the American Industrial Hygiene Association Laboratory Accreditation Program, for analysis following relevant standard methods. The respirable dust samples were analyzed according to NIOSH Method 0600 (NIOSH, 1998). Crystalline silica analysis for the samples was performed using XRD according to NIOSH Method 7500 (NIOSH, 2003) including analyzing a bulk dust sample of each stone type first for an interference check. All the samples from the same stone type and grinding time were divided into two groups consistently, with one group using muffle furnace ashing preparation and the other group using THF dissolution preparation so that their results could be compared. See supplementary material for details of the analytical equipment and solutions. Three samples for each of the two methods were collected for analysis when grinding 1, 2, and 4 min; and six samples for each of the two methods were collected when grinding 8 min. The paste-like residue was indeed observed for all the samples using THF but the amount was significantly greater for samples collected from the engineered stone compared to those from the granite. Extra THF was used to rinse the residue onto the silver membrane filter for subsequent XRD analysis.

Results and discussions

We calculated the crystalline silica content (as a percentage by weight) for each sample by computing the ratio of the masses of crystalline silica and respirable or bulk dust. The bulk dust from the granite stone was 30% crystalline silica with quartz being the only crystalline silica polymorph detected. The bulk dust from the engineered stone was 60% crystalline silica with 14% being the quartz polymorph and 46% the cristobalite polymorph (see additional details in Supplementary Information). Figure 1 is a plot of the resulting crystalline silica content from the respirable dust samples of the two stone types using the two sample preparation methods.

The *X*-axis of Fig. 1 reports the average masses of respirable dust from at least three samples for each data point, with the horizontal error bars representing one standard deviation of the respirable dust mass for the corresponding sample sets. For each stone type and preparation method, four data points are illustrated with different masses of respirable dust deposited due to different grinding times. Overall, the samples collected with the same grinding times of the same stone type had similar amounts of respirable dust (see additional details in Supplementary Information). The variations can mainly be attributed to the fact that samplers located at different positions in the flow splitting apparatus experienced different particle losses.

The *Y*-axis of Fig. 1 reports the average crystalline silica content with the vertical error bars representing the combined standard uncertainties for each data point (see Supplementary Information on definition and derivation). For samples of dust produced while grinding the piece of granite, the two preparation methods resulted in similar crystalline silica content for all four levels of respirable dust loading. As hypothesized, statistical analysis of a *t*-test (one-tailed and heteroscedastic) showed that the difference between the two methods for the granite dust samples was not significant ($P \geq 0.05$, see Table 1). For the engineered stone dust samples, the two methods had closer crystalline silica content for the two higher respirable dust loading levels, and their differences were not statistically significant

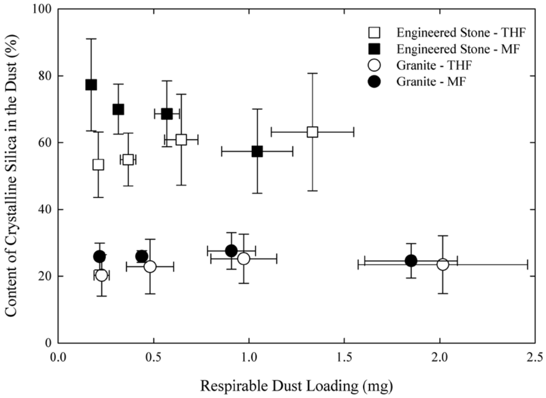

Figure 1. Content of crystalline silica in the respirable dust collected from grinding engineered stone or granite. The samples were prepared using either tetrahydrofuran (THF) or muffle furnace (MF).

Downloaded from https://academic.oup.com/annweh/article/66/9/1210/6692700 by Centers for Disease Control user on 15 November 2022

Table 1. Statistical analyses of the comparison of the crystalline silica content between samples prepared by using muffle furnace and tetrahydrofuran (THF): *P* value for each comparison .

	Grinding time 1 min	Grinding time 2 min	Grinding time 4 min	Grinding time 8 min
Engineered stone (crystalline silica)	0.001	0.001	0.09	0.11
Engineered stone (quartz)	0.002	<0.001	0.03	0.48
Engineered stone (cristobalite)	<0.001	0.002	0.14	0.12
Granite (crystalline silica)	0.05	0.08	0.05	0.18

(see Table 1); however, the crystalline silica content of samples from using THF dissolution was significantly lower (P = 0.001) than that of the counterpart samples from using muffle furnace ashing for the other two lower respirable dust loading levels. Specifically, for the samples from grinding 1 and 2 min of the engineered stone (which produced average respirable dust loading of about 0.19 and 0.34 mg, respectively), the crystalline silica content of the samples from using THF dissolution was 30.9 and 21.5% lower than that of the counterpart samples from using muffle furnace ashing, respectively. Note that the respirable dust samples from the engineered stone contained both quartz and cristobalite with a similar distribution among the two polymorphs as observed in the corresponding bulk dust sample. Supplementary Fig. S2 in the Supplementary Information presented the average quartz and cristobalite contents from the respirable dust samples of the engineered stone using the two sample preparation methods, which follow the same trend as the total crystalline silica content shown in Fig. 1. Table 1 also lists the *P* values when comparing the quartz and cristobalite contents of the respirable dust samples of the engineered stone using the two sample preparation methods. The results are consistent with those from comparing the total crystalline silica content.

These results demonstrate that using THF dissolution to process RCS samples from engineered stone can lead to significantly lower quantification of crystalline silica content in the samples. The particle loss from the paste-like residue formed from the reactions between THF and the resins likely contributed the most to the lower quantification. As mentioned above, a significant amount of residue was formed when using THF dissolution to process the samples collected from grinding the engineered stone. Although extra THF was used to rinse and recover the residue, it is likely that the recovery was incomplete, especially if the residue formed thin layers on the apparatus and failed to be rinsed off. After the recovery effort for samples with different dust loading levels, it is possible that the remaining particle loss was from the residual failed to be rinsed off and was in similar amount. Therefore, the amount of lost particles would represent a smaller percentage of the dust loading on the samples with higher masses of respirable dust (>0.5 mg), leading to negligible effects on the silica content results as shown in Fig. 1. However, among samples with respirable dust masses less than 0.5 mg, the similar amount of particle loss represents a higher percentage of the dust loading and can lead to significantly lower quantification of crystalline silica.

Laboratories that are not aware of this issue may not perform the extra rinse and recovery procedures for the residue when using THF dissolution to prepare the samples, likely leading to even lower quantification of crystalline silica across all ranges of respirable dust loading on filter samples. Most full-shift samples from field surveys in this industry are expected to have respirable dust levels below 0.5 mg. As an example, assuming using a sampler with a flowrate of 2.5 L min^{-1} to collect 480 minutes of air that has an RCS concentration of 0.05 mg m^{-3} (OSHA PEL) and a 60% silica content (similar to the levels reported in Fig. 1), the calculated respirable dust on the filter is 0.1 mg. Therefore, most field assessment on workers' RCS exposure in the stone countertop industry could be affected by using THF to process samples for XRD analysis.

Note that the variations of crystalline silica content are larger in the engineered stone than in the granite, which is likely due to the heterogeneous distribution of crystalline silica in the engineered stone. There appears to be a small trend on silica content among different dust loading levels from the two methods for the engineered stone. However, the small trend is more likely due to the heterogeneous distribution of crystalline silica in the engineered stone as well, especially considering that the four data points with their vertical error bars, representing combined standard uncertainty, are well overlapped. Using an engineered stone with more homogeneous silica distribution, if available, and/or increasing the sample size (both dust loading levels and samples at each dust loading level) may lead to more conclusive results on this observation, but it is beyond the scope of this study.

Conclusions

When conducting assessments on workers' RCS exposures in the stone countertop industry, extreme caution

Downloaded from https://academic.oup.com/annweh/article/66/9/1210/6692700 by Centers for Disease Control user on 15 November 2022

should be exercised when using THF for sample preparation which may lead to significantly lower quantification of the RCS in the air samples. Although the RF plasma ashing method was not investigated in this study, it does not react with resins, thus, it would be expected to work similarly to muffle furnace. Either muffle furnace or RF plasma ashing should be specified as the preferred processing method when engineered stone is expected to present in the sampling location to produce more accurate quantification of crystalline silica.

Supplementary Data

Supplementary data are available at *Annals of Work Exposures and Health* online.

Funding

National Institute for Occupational Safety and Health project [Engineering Control of Silica Dust from Stone Countertop Grinding and Polishing (CAN# 927ZLHK)]. This project was supported in part by an appointment to the Research Participation Program at the Centers for Disease Control and Prevention, administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and CDC.

Conflict of interest

All authors declare no conflicts of interest.

Disclaimer

The findings and conclusions in this report are those of the author(s) and do not necessarily represent the official position of the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention. Mention of any company or product does not constitute endorsement by the National Institute for Occupational Safety and Health, Centers for Disease Control and Prevention.

Data Availability

The data underlying this article will be shared on reasonable request to the corresponding author.

References

CFR. (2016) *29 CFR 1926.1153. Code of Federal Regulations*. Washington, DC: U.S. Government Printing Office, Office of the Federal Register.

Friedman GK, Harrison R, Bojes H *et al*. (2015) Notes from the field: silicosis in a countertop fabricator—Texas, 2014. *Morb Mortal Wkly Rep*; **64**: 129–30.

Hoy RF, Baird T, Hammerschlag G *et al*. (2018) Artificial stone-associated silicosis: a rapidly emerging occupational lung disease. *Occup Environ Med*; **75**: 3–5.

Kang S, Qian Y, Liang H *et al*. (2019) The composition of emissions from sawing Corian®, a solid surface composite material. *Ann Work Expo Health*; **63**: 480–3.

Kramer MR, Blanc PD, Fireman E *et al*. (2012) Artificial stone silicosis: disease resurgence among artificial stone workers. *Chest*; **142**: 419–24.

NIOSH. (1998) *Particulates not otherwise regulated, respirable: Method 0600. NIOSH Manual of Analytical Methods (NMAM®), Issue 3*. National Institute for Occupational Safety and Health. Available at https://www.cdc.gov/niosh/docs/2003-154/pdfs/0600.pdf. Accessed 8 February 2022.

NIOSH. (2003) *Silica, crystalline, by XRD (filter redeposition): Method 7500. NIOSH Manual of Analytical Methods (NMAM®), Issue 4*. National Institute for Occupational Safety and Health. Available at https://www.cdc.gov/niosh/docs/2003-154/pdfs/7500.pdf. Accessed 8 February 2022.

NIOSH. (2016) *Evaluation of Crystalline Silica Exposure during Fabrication of Natural and Engineered Stone Countertops*. By Zwack LM, Victory KR, Brueck SE, Qi C. HHE Report No. 2014-0215-3250.

OSHA. (2016) *OSHA method ID–142. Crystalline silica quartz and cristobalite*. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration. Available at https://www.osha.gov/sites/default/files/methods/id142.pdf. Accessed 30 June 2022.

OSHA. (2020) *OSHA's National Emphasis Program—respirable crystalline silica*. Washington, DC: U.S. Department of Labor, Occupational Safety and Health Administration, OSHA Instruction, Directive No. CPL 03–00–023. Available at https://www.osha.gov/sites/default/files/enforcement/directives/CPL_03-00-023.pdf. Accessed 8 February 2022.

Pascual S, Urrutia I, Ballaz A *et al*. (2011) Prevalence of silicosis in a marble factory after exposure to quartz conglomerates. *Arch Bronconeumol*; **47**: 50–1.

Pérez-Alonso A, Córdoba-Doña JA, Millares-Lorenzo JL *et al*. (2014) Outbreak of silicosis in Spanish quartz conglomerate workers. *Int J Occup Environ Health*; **20**: 26–32.

Qi C, Echt A, Gressel M. (2016) On the characterization of the generation rate and size-dependent crystalline silica content of the dust from cutting fiber cement siding. *Ann Occup Hyg*; **60**: 220–30.

Qi C, Echt A, Lo L. (2017) Exposure to Respirable Crystalline Silica during Stone Countertop Grinding/Polishing using Handheld Tools. The 36th Annual Conference of American Association for Aerosol Research, October 16–20, 2017; Raleigh, NC. https://www.aaar.org/2017/

Ronsmans S, Decoster L, Keirsbilck S *et al*. (2018) Artificial stone-associated silicosis in Belgium. *Occup Environ Med*; **76**: 133–4.

Rose C, Heinzerling A, Patel K *et al*. (2019) Severe silicosis in engineered stone fabrication workers—California, Colorado, Texas, and Washington, 2017–2019. *MMWR Morb Mortal Wkly Rep*; **68**: 813–8.

Downloaded from https://academic.oup.com/annweh/article/66/9/1210/6692700 by Centers for Disease Control user on 15 November 2022