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Original Article

Compatibility of engineered stone materials with tetrahydrofuran processing for crystalline silica analysis by XRD

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Abstract

This study investigated the compatibility of Tetrahydrofuran (THF) dissolution, following the procedures outlined in NIOSH Method 7500 and the similar OSHA ID-142 method, as a sample preparation technique for respirable crystalline silica (RCS) analysis in engineered stone materials compared to the muffle furnace (MF) ashing method. Our results revealed considerable variability in RCS content across different batches of engineered stone tested, underscoring the inherent material heterogeneity in engineered stone products. A statistically significant underestimation of RCS concentrations was observed when using THF dissolution for Stone A (polyester-based) samples collected on 47 mm polyvinyl chloride (PVC) filters, particularly at lower analyte loadings. In contrast, no statistically significant differences in RCS measurement were found between THF dissolution and MF ashing for the other 3 stone types, including one laboratory-synthetic material. The observed discrepancy in Stone A is likely attributed to the interaction of THF with its polyester resin binder, leading to swelling of the filter matrix and forming a non-volatile residue. This residue may physically entrap silica particles, hindering their complete recovery and subsequent quantification by X-ray diffraction (XRD). The suitability of THF processing as a sample preparation method is therefore highly dependent on the specific composition of the engineered stone. Based on these findings, MF ashing is recommended as the more reliable and universally applicable sample preparation method for engineered stone samples, especially those containing polyester resin binders. Caution should be exercised when considering THF dissolution for RCS analysis in engineered stones due to the potential for significant underestimation of actual RCS values, which could have implications for exposure assessments and regulatory compliance.

Keywords: crystalline silica; engineered stone; tetrahydrofuran; X-ray diffraction

What's Important About This Paper?

This study investigates the compatibility of tetrahydrofuran dissolution as a sample preparation technique for crystalline silica analysis by XRD for engineered stone materials compared to the muffle furnace ashing method. The results confirmed that the suitability of tetrahydrofuran processing is highly dependent on the specific composition of the engineered stone, such that muffle furnace ashing is recommended as the more reliable and universally applicable, especially for engineered stones containing polyester resin binders. This finding is critically important for selecting a proper method to measure respirable crystalline silica exposure in the stone countertop industry, which has been experiencing a global silicosis outbreak.

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Introduction

Engineered stone, also known as artificial stone, has experienced a significant surge in popularity over recent decades, becoming a dominant material in construction and interior design, particularly for kitchen and bathroom countertops (Freedonia Group 2022). Most engineered stones are composite materials typically formulated with high proportions of crystalline silica, primarily quartz and sometimes cristobalite, often exceeding 70% and even 90% by weight, which significantly exceeds that of natural stones like granite, which typically contain 30% to 50% (Carrieri et al. 2020; Hall et al. 2021) The material consists of silica particles bound with polymeric resins (eg unsaturated polyester, acrylic, epoxy, etc.) and various pigments and additives to enhance specific properties (Carrieri et al. 2020; Hall et al. 2021; Thompson and Qi 2023). Processes such as cutting, grinding, and polishing generate substantial amounts of airborne dust that contains high concentrations of respirable crystalline silica (RCS) small enough to penetrate deep into the gas-exchange regions of the lungs when inhaled (Kramer et al. 2012; Hoy et al. 2018; Leso et al. 2019; Mandler Qi and Qian 2022). The widespread use and fabrication of engineered stone have presented significant occupational health hazards. Silicosis outbreaks and case series have been identified in the United Kingdom, China, Spain, Italy, Belgium, Australia, and the United States (Kramer et al. 2012; Pérez-Alonso et al. 2014; Friedman et al. 2015; Kirby 2019; Ronsmans et al. 2019; Rose et al. 2019; Heinzerling et al. 2020; Wu et al. 2020; Salamon et al. 2021; Surasi et al. 2022; Barber 2024; DeVaughn et al. 2025). Given the severe health risks associated with exposure to RCS, accurate assessment and quantification of RCS are essential for effective risk management, ensuring compliance with occupational exposure limits and action levels established by the Occupational Safety and Health Administration (OSHA) (OSHA and NIOSH 2015; OSHA 2016b). The reliability of analytical methods used for RCS quantification is therefore a critical component for exposure assessment.

In the United States, the National Institute for Occupational Safety and Health (NIOSH) Method 7500 is a widely recognized standard method for quantitatively determining crystalline silica polymorphs in workplace air samples. The method utilizes X-ray Diffraction (XRD) for analysis, which allows for the differentiation of the crystalline polymorphs from their characteristic X-ray diffraction patterns. A crucial step before XRD analysis is removing the PVC filter matrix by ashing with a muffle furnace (MF), low-temperature plasma ashing (LTA), or dissolution in Tetrahydrofuran (THF). Notably, the OSHA ID-142 method (OSHA 2016a) follows a similar procedure that also uses THF for filter dissolution. After removing the PVC content, the suspended particulate matter (including RCS) is subsequently redeposited onto a silver membrane filter for XRD analysis. The accurate measurement of RCS by XRD can be influenced by several analytical factors, such as particle size variations, limited X-ray penetration depth, and the attenuation of the diffraction signal by other substances in the sample matrix (Hurst Schroeder and Styron 1997; Chen et al. 2014; Rishi et al. 2024). Interferences may also occur during sample preparation, which can lead to inaccuracies in the results.

Previous studies(Eller et al. 1999) indicated no significant differences in RCS quantification among the 3 preparation methods: MF, LTA, and THF. However, a recent study(Qi Thompson and Amy Feng 2022) has raised concerns about the compatibility of THF processing with specific engineered stone dust samples. The results revealed that for one particular type of engineered stone, referred to as "Stone A," the quartz content measured after THF filter dissolution was significantly underreported (up to 20% to 30% lower) compared to measurements obtained using muffle furnace ashing, especially at low dust loadings. It is hypothesized that interactions between THF and the resin binders in the engineered stone may cause silica to be lost or rendered undetectable. As a result, using THF for such samples is cautioned to avoid artificially low RCS values. This finding suggests that THF may not be suitable for engineered stone materials, particularly those quartz-rich and resin-bound, like the Stone A type, potentially affecting the accuracy of RCS measurements. However, this study was limited to a single type of engineered stone. It highlighted the need for confirmation across various engineered stone materials and through more specifically designed experiments to probe the underlying causes of the observed discrepancy of using THF and MF processing. Therefore, the objective of the present study was to systematically evaluate the compatibility of THF processing with different engineered stone materials for XRD analysis by the NIOSH method 7500.

In the present study, we evaluated several factors that could impact the compatibility of THF processing and RCS measurement for engineered stone samples. (i) Heterogeneity of Materials. The inherent variability in silica content within or between batches of tested engineered stones can significantly contribute to measurement inconsistency, regardless of the sample preparation method. (ii) Stone Types. The components of different engineered stone products, including their resin binders, crystalline silica content, additives, and fillers, can differ considerably. Soluble and interacting substances in the stone can complicate chemical dissolution, consequently introducing uncertainty in silica measurement. (iii) Filter Dissolution in THF.

Incomplete dissolution of the PVC filter in THF, potentially exacerbated by factors like larger filter sizes (eg 47 mm) or high concentration of interacting resin components, may lead to residue formation and analyte loss during processing. (iv) THF-Resin Interaction. Chemical or physical interactions occur specifically between THF and specific engineered stone components, particularly the resin binder (eg cured polyester or other components). These interactions can cause resin swelling, formation of insoluble or partially soluble residues, or gelation, leading to incomplete recovery or interference during the analysis, resulting in mass loss and underestimated RCS values. All the above factors will lead to uncertainties when processing with THF and redeposition on silver membrane filters.

Materials and methods

Materials

In this study, we tested dust samples generated from 3 commercially available engineered stones and one laboratory-synthetic material. The samples were collected on various sizes of PVC filters. We compared 2 sample preparation methods: THF dissolution and MF ashing, for subsequent XRD analysis following NIOSH Method 7500 (NIOSH 2003). Three types of engineered stone were selected to represent a range of compositions. Stone A contains about 70% to 90% crystalline silica, as specified by the manufacturer, and is bonded with polyester resin and pigments. This material is identical to the "Stone A" category described in the previous study (Qi et al. 2022). It is expected to exhibit possible incompatibility with THF due to its high quartz and resin content. According to the manufacturer, Stone B is produced with a new formula that reduces the crystalline silica content to less than 50% and uses polyester resin as a binder. Stone C is an acrylic polymer-based material containing a reduced silica content. Dust samples were obtained from a stack of multiple distinct slabs or a large block of these materials. A laboratory-synthesized resin was prepared using a commercially available polyester resin for stones (Tenax Mastic, free-flowing type) mixed with a hardener. To simulate an engineered stone with varying resin content, a mixture was prepared using sanding dust from cured resin blocks combined with National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 1878b in a specified weight ratio. SRM 1878b (α-Quartz) and SRM 1879b (Cristobalite) were used for XRD instrument calibration.

Sample generation and collection

To ensure controlled and comparable samples, dust was generated from bulk pieces of Stones A, B, and C using a laboratory grinding apparatus housed within a controlled environmental chamber, similar to setups described in previous publications (Qi Echt and Gressel 2016; Qi et al. 2022; Thompson and Qi 2023; Rishi et al. 2024). Aerosol was generated within the test chamber by manually grinding a stack of engineered stone samples. All grinding was performed on dry surfaces without applying water. This was accomplished using a handheld pneumatic angle grinder (Gison Machinery Co., Ltd., Model GPW-216) fitted with a 10 cm diameter, coarse, diamond grinding cup wheel (Stone Industrial Supplies, Inc., Model SIS-4SPCW-SC). Multiple respirable dust samples were collected concurrently from the airborne dust cloud via a sampling probe on the duct. Further details regarding the system's operation and the sampling procedures can be found in the Supplementary Information of prior publications (Qi et al. 2022; Rishi et al. 2024). GK 4.162 RASCAL Cyclones (Mesa Laboratories, Inc., USA), operating at a flow rate of 9.0 L/min, were employed to collect respirable dust from Stones A, B, and C on 47 mm diameter, 5 μm pore size PVC filters (SKC Inc., Part# 225-5-47), backed by cellulose support pads within 3-piece conductive cassettes. Additionally, another set of aerosol samples from Stone A was collected using 3-piece cassettes attached to a GK2.69 cyclone, which operated at 4.2 L/min to capture respirable particles on 25 mm, 5 μm pore size PVC filters (SKC Inc., Part# 225-5-25). Testing and sampling times were varied to achieve different target mass loadings on the filters.

After completing the grinding tests in the test chamber, the settled dust from Stone A, a composite "bulk" sample, was carefully collected. This dust was then suspended in Isopropanol (Sigma-Aldrich, ACS reagent grade) to be dispensed onto various sizes of PVC filters. The objective was to evaluate the impact of PVC content on the THF dissolution and XRD analysis. A fixed amount of the Stone A dust from a stock suspension (about 1 mg) was applied to 25 mm, 37 mm, and 47 mm (2 different lots) diameter PVC filters with a pore size of 5.0 μm (SKC Inc, Part# 225-5-25, 225-5-37, 225-5-47). Blank PVC filters were also prepared to test the baseline residue level after THF and MF treatments.

Resin particulates for a stock suspension were obtained by lightly sanding cured laboratory-synthesized polyester resin blocks using 600-grit sandpaper. The collected dust was then dispersed in Isopropanol to create a suspension with a known resin concentration. To simulate engineered stone samples with varying resin content, a fixed quantity of Quartz (SRM 1878b, 500 μg) was mixed with specific amounts of resin from prepared stock suspension and applied to 25 mm and 47 mm, 5 μm pore size PVC

filters. The resin levels on these filters were set at the ratios of resin/SRM = 0.2, 1, and 2, with triplets prepared for each level. Using spiked filters ensured we had precise control over silica quantity and resin composition, and could directly compare recovery by each preparation method.

Sample treatment and XRD analysis

Collected filters from the same stone type and collection method (aerosolized or spiked) were randomly assigned to 2 groups for the dissolution or ashing pathway. Three samples for each of the 2 methods were collected for analysis. Following NIOSH method 7500 guidelines, PVC filters were dissolved in Tetrahydrofuran (Sigma-Aldrich, HPLC-grade) or ashed using a Muffle Furnace (Thermo Scientific, Model FB1400). The residues were then redeposited on 25-mm, 0.45 μm pore size silver membrane filters (Sterlitech, Part# 45335). Several observation points were established to visually inspect the residue levels during sample preparation. Detailed sample preparation procedures can be found in the Supplementary Information S.1.

The silver membrane filters containing the deposited samples were mounted onto holders with a "zero background" backing plate made of silicon single crystal. The samples were analyzed with an X-ray Diffractometer (PANalytical, Model Empyrean II) operated at 45 kV and 40 mA, with a 1.8 kW long fine focus Cu X-ray tube. The net peak area for each silica polymorph at the primary angle (26.7° for α-Quartz and 21.9° for Cristobalite) was measured using a slow-step scan (0.01 °2θ/step), with Bragg–Brentano HD optics and PIXcel 3D detector. The net intensity was then normalized using a reference specimen to compensate for long-term drift in X-ray tube intensity. Silica polymorphs were quantified according to the NIOSH method 7500, utilizing standards SRM 1878b and 1879b for calibration.

Gravimetric measurements

Filter media underwent overnight conditioning in a humidity-controlled environment before initial weighing. Following sample deposition, the media were dried at 30 to 40 °C for 2 h and returned to the humidity chamber for reconditioning. A 7-digit microbalance (Mettler Toledo, Model XPR6U) was used to perform pre- and post-gravimetric analyses. Each filter was weighed 3 times, before and after the experiment, with the average weight difference representing the deposited mass. Gravimetric measurements were conducted under the following environmental conditions: temperature of 23 °C (±1.5), pressure of 749 mm Hg (±5), and humidity of 35% (±17).

Experimental design

Key elements of the experimental design included aerosol sample collection on filters, spiking of filters with a known amount of dust, and parallel analysis by the 2 methods with statistical comparison of the resulting RCS measurements. Commercial products with polyester binders (Stone A and B, varying in silica concentration) and an acrylic-based (Stone C) were tested. This aimed to determine if product formulation, specifically resin type and concentration, contributes to observed residue issues. Given prior observations of residue formation with Stone A and significant RCS measurement differences between THF and MF, experiments were specifically designed to examine how residue formation in Stone A varies with different material batches and PVC filter sizes used for sample collection. Laboratory-synthesized samples with a known composition serve as an additional reference. Tests were conducted on mixtures with measured amounts of SRM and polyester resin dust to assess how varying resin content affects silica recovery. The mass deposited on PVC and silver membrane filters before and after applying THF/MF procedures was measured gravimetrically. This analysis aims to quantify residue levels resulting from 2 preparation methods and assess the influence of variables such as resin content and PVC filter size on silica measurements.

Specific procedures were implemented in the experiment to address the study hypotheses directly: (i) Heterogeneity. Samples generated by grinding Stone A, which were sourced from different batches, were analyzed using the THF and MF preparation method. The measured RCS content was calculated and compared to evaluate the impact of material variability. (ii) Stone Type. Samples were generated by grinding Stone B and C in the same experimental setup to compare with Stone A. (iii) Filter Dissolution. During the THF preparation steps (see Supplementary Information), visual comparisons of dissolution completeness were systematically made between 25 mm, 37 mm, and 47 mm PVC filters for blanks and loaded samples. Observations regarding residue formation, swelling, gelation, discoloration, and filtration difficulties were documented. (iv) THF-Resin interaction. In addition to qualitative observation, gravimetric assessment was performed before and after THF/MF treatments to quantify the non-volatile residue formed from the stone's undissolved PVC and/or resin binder materials.

Results and discussion

Heterogeneity of materials

Variability in RCS content is anticipated across multiple samples obtained under identical experimental conditions from different batches of the sample material.

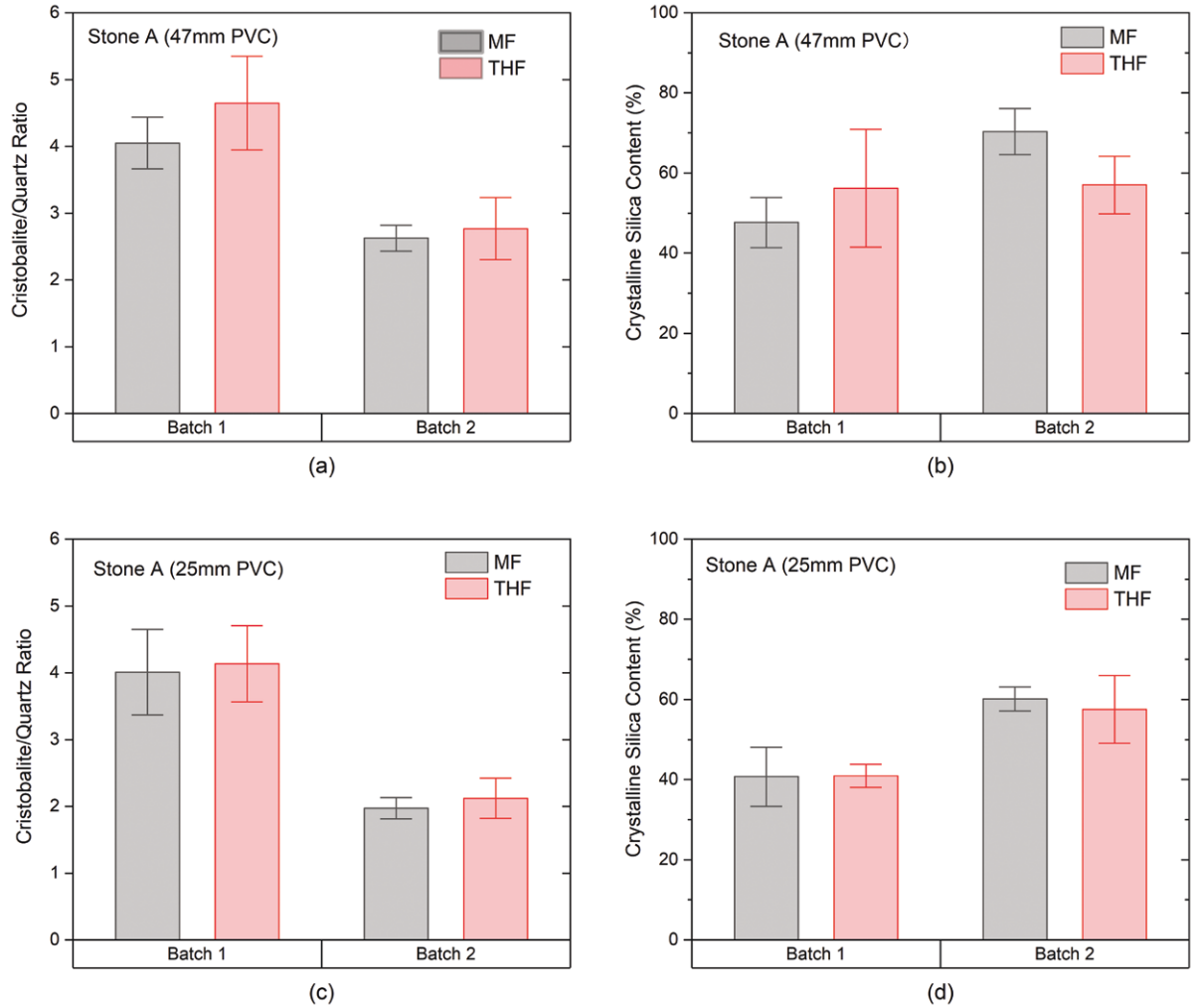

Fig. 1. Comparison of the Cristobalite/Quartz ratio (R_{cq}) and the total crystalline silica content (wt%) in aerosol samples of Stone A, collected on PVC filters, with either MF or THF pre-treatment. Panels (a) and (b) display data from 47 mm PVC samples collected from 7 stacks of substrates from different production batches of Stone A. Panels (c) and (d) show results from 25 mm PVC samples taken from Batch 1 (conducted on a stack of the 7 substrates) and Batch 2 (performed on a block) of Stone A, respectively.

This expected variation arises from the inherent heterogeneity of the engineered stone materials, where the distribution of silica within the polymer matrix can differ between batches and even within the same batch. This is particularly evident when the sample volume is too small to reflect the material's overall properties accurately (Hall et al. 2021). The objective was to determine if significant batch-to-batch differences exist within each filter size group and to evaluate whether the processing method (MF vs. THF) consistently affects the measured Silica% and Cristobalite-Quartz ratio under these distinct collection conditions. Two-way analyses of variance (ANOVA) were conducted to assess the main effects of batch (1 vs. 2) and process (MF vs. THF), as well as their interaction effect. ANOVA assumptions (normality of residuals via Shapiro-Wilk test, homogeneity of variance via Levene's test) were checked for each model. Statistical significance was assessed at 0.05. Details of the statistical analysis can be found in the Supplementary Information S.2.

Figure 1 compares the Cristobalite-Quartz ratio (R_{cq}) and silica content (wt%) for Stone A dust samples collected on 47 mm and 25 mm filters. Significant batch differences of R_{cq} were consistently observed regardless of filter size ($P = 0.0002$ for 47 mm and $P < 0.0001$ for 25 mm), indicating the significant compositional differences between batches. For 25 mm filters, the effect of process and process-batch interaction

was insignificant. For 47 mm filters, the batch effect on silica content was complex and intertwined with the processing method, as indicated by the significant interaction term of process and batch ($P = 0.014$). This indicates the potential impact of using a larger filter on RCS measurement.

The analysis was also performed to assess the effect of the process method (MF vs THF) on Silica% for Stone A samples. It does not support the conclusion that THF generally produces different results than MF across the board. For 25 mm filters, no significant difference between MF and THF was found for Silica%. For 47 mm filters, while a significant main effect of the process was found for Silica% ($P = 0.018$), it was qualified by a significant interaction with batch ($P = 0.014$). This means the difference between MF and THF for 47mm Silica% measurements depends on which batch is considered. When only analyzing the dataset for 47 mm filters in Batch 2, the MF process resulted in significantly higher measured Silica% on average than the THF process. This is consistent with previous study results (Qi et al. 2022). The Welch's *t*-test comparing Silica% for MF (mean = 67.9%) and THF (mean = 55.6%) yielded a *P*-value of 0.0036. No significant process effect was found for the R_{cq}, suggesting the compositional changes within the batch are minimal.

Analyzing the polyester-based engineered stone (Stone A) reveals significant variability between batches, significantly affecting silica measurements. The processing method (MF vs THF) generally had an insignificant impact, except when measuring silica content on 47 mm filters, where its influence varied depending on the experimental batch. In samples from the same batch (eg Batch 2 in this study), a significant difference between MF and THF was observed. These findings highlight the critical need to consider batch effects in experimental design and investigate how filter size affects the THF process.

Stone types and mass loadings

Three commercially available engineered stone samples with varying silica content and resin compositions were selected for quantitative comparison: Stone A (high crystalline silica, polyester binder), Stone B (reduced crystalline silica, polyester binder), and Stone C (moderate crystalline silica, acrylic-based binder). The samples from the same batch were collected on 47 mm PVC filters under similar experimental conditions, processed by MF and THF, and analyzed by XRD following the NIOSH method 7500.

Crystalline silica content (%) for Stone A, B, and C samples collected on 47 mm filters is compared in Fig. 2a. Independent *t*-tests (Welch's) were performed to evaluate the effects of MF and THF processes. A significant difference (P=0.0036) in crystalline silica content was found for Stone A, with MF (67.9% ± 9.5%) yielding higher results than THF (55.6% ± 8.0%). In contrast, no significant differences were observed for Stone B ($P = 0.0675$) and Stone C ($P = 0.2779$). MF-processed samples consistently showed higher crystalline silica content across all stone types.

The relationship between mass loading and measured silica content for Stone A was assessed. Figure 2a shows the silica content analysis across different mass ranges for MF and THF processing methods. Table 1 presents the mean RCS% values for Stone A and their statistical significance at various loading levels. The data indicate that the statistically significant

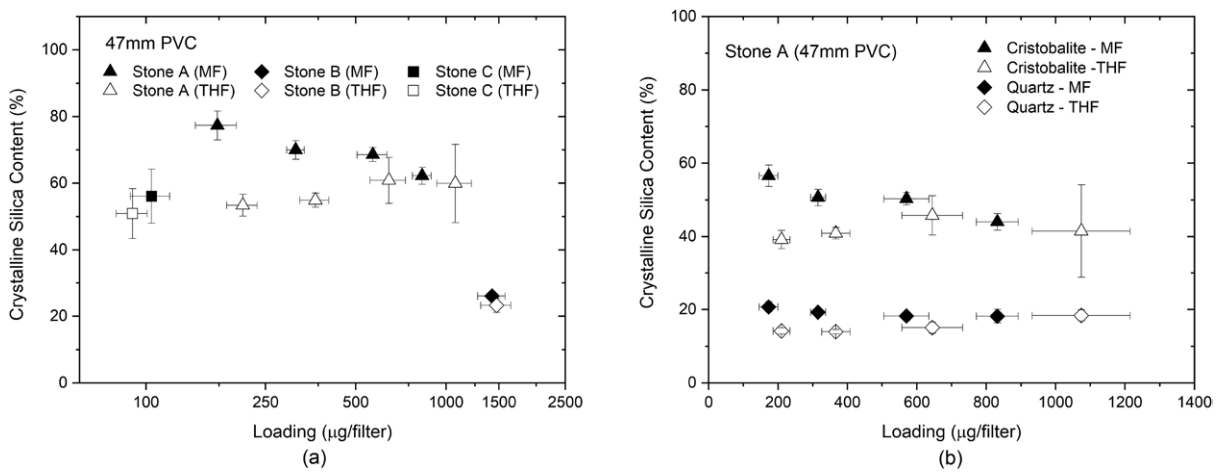

Fig. 2. Comparison of (a) total crystalline silica content (wt%) in aerosol samples collected on 47 mm PVC filters from Stones A, B, and C, which were pre-treated with either MF or THF. (b) The content (wt%) of Cristobalite and Quartz in aerosol samples from Stone A as a function of loading levels.

Table 1. Comparison of MF vs THF for crystalline silica measurement for Stone A on 47 mm PVC filters. *P*-values are shown with significance markers (*$P < 0.05$, (ns) $P >= 0.05$).

Loading Level (µg/filter)	RCS% by MF Mean (SD)	RCS% by THF Mean (SD)	Significance *P*-value
Low (<250)	77.3 (4.3)	53.4 (3.3)	0.0020*
Moderate (250–500)	69.7 (2.4)	54.9 (2.1)	0.0005*
High (500–1000)	65.8 (3.9)	60.9 (6.9)	0.3493 (ns)
Very High (>1000)	47.7 (6.3)	57.7 (13.5)	0.2038 (ns)

difference, where MF produces higher silica content than THF, is mainly observed at lower to moderate sample mass loadings (below 500 µg). The difference between the 2 processes was not statistically significant at higher mass loadings. The observed variability may arise from the heterogeneity of the materials within the tested sample stack. Analyzing small volumes (with low mass loading) could cause samples that do not accurately represent the overall material composition, especially concerning the varying levels of resin content that may affect the effectiveness of the THF process.

The silica polymorphs in Stone A were analyzed to determine which analyte exhibits a stronger response to the THF method. As shown in Fig. 2b, the samples treated with THF consistently displayed lower silica content than those treated with MF. Notably, Cristobalite demonstrated a higher sensitivity to the THF process than Quartz, especially at low to moderate loadings (below 500 µg). The differences observed between the MF and THF treatments were statistically significant for Cristobalite at these lower loadings ($P \approx 0.0002$), in contrast to Quartz ($P \approx 0.0008$).

PVC filter dissolution

Previous work (Qi et al. 2022) has indicated potential issues with using THF to process engineered stone samples (Stone A) collected on 47 mm filters. It reported a "paste-like residue" consistently formed during the THF process. Incomplete PVC dissolution and possible interactions between THF and the engineered stone's resins are suspected to cause particle loss and artificially lower silica content measurements. Therefore, we evaluated the effectiveness of THF dissolution on standard PVC filter sizes (25 mm, 37 mm, and 47 mm from 2 lots) using both blank and dust-loaded filters. Throughout the THF processing and redeposition stages, we qualitatively assessed residue formation at each step. The net residue levels for different filter sizes were determined by gravimetrically measuring the weight of the silver membrane filters before and after the redeposition.

Following a modified THF process based on NIOSH method 7500 (see Supplementary Information), all filters were completely dissolved in 10 mL of THF with sonication and then transferred to silver membrane filters. For the 25 mm, 37 mm, and 47 mm Lot A filters, filtration times increased gradually but remained under 30 seconds. However, the 47 mm Lot B filters (which had the highest PVC content and were used in a prior study) exhibited significantly longer filtration times, suggesting potential undissolved PVC residue and other additives. Unlike THF, MF-processed filters showed consistent filtration times regardless of filter mass. As shown in Table 2, the percentage of remaining residue after treatment remains consistent across various filter sizes for a given treatment. For instance, treatment with THF results in approximately 1% residue from blanks, which is ten times greater than the approximately 0.1% residue observed with MF. This suggests that MF is a more effective method for removing PVC content.

To examine the interaction of engineered stone dust with PVC during THF treatment, approximately 1 mg of Stone A settling dust (collected from the grinding tests) was added to PVC filters of varying sizes. All filters were fully dissolved in 10 mL THF using sonication. A cloudy and slightly discolored suspension was noted for samples prepared on 47 mm (Lots A and B) filters. After adding more THF during rinsing, the filtration and redeposition were completed. The entire filtration time for 25 mm and 37 mm filters was under 30 s, whereas all 47 mm samples required over 300 s. The deposited silver membrane filters from the 47 mm samples displayed viscous residues, consistent with previous findings (Qi et al. 2022). MF-treated samples were all successfully redeposited on silver membrane filters without issues. Regardless of filter size, their filtration times were comparable, each taking under 30 s.

Figure 3a compares crystalline silica content in spiked Stone A samples using PVC filters of various sizes (25 mm, 37 mm, 47 mm-Lot A, and 47 mm-Lot B) relative to reference lines indicating Quartz (13.5%), Cristobalite (46.7%), and total silica (60.2%) in the

Table 2. Mean residue level (wt%) and filtration time (s) of blank PVC filters (25 mm, 37 mm, 47 mm Lot A, 47 mm Lot B) using THF and MF processes. For the MF process, ashed samples were resuspended in isopropanol and redeposited onto silver membrane filters using the same filtration setup as the THF process.

		THF		MF	
PVC Filter	Mass (mg)	Residue (%)	Filtration Time (s)	Residue (%)	Filtration Time (s)
None	-	-	10	-	37
25 mm	5.6	1.1%	15	0.2%	44
37 mm	11.7	1.1%	20	0.1%	44
47 mm A	16.1	0.9%	25	0.1%	45
47 mm B	22.8	0.9%	130	0.1%	45

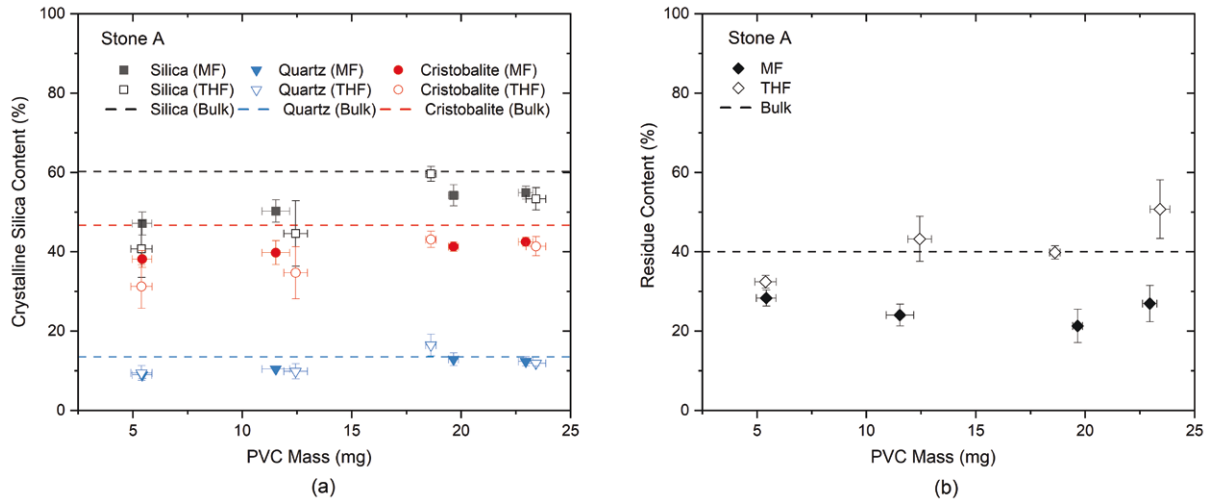

Fig. 3. (a) Comparison of the crystalline silica content (wt%) in Stone A samples, which were spiked on 25 mm, 37 mm, 47 mm (Lot A), and 47 mm (Lot B) filters, using either MF or THF pretreatment methods. The reference lines show the silica content of the bulk Stone A dust: Quartz (13.5%), Cristobalite (46.7%), and total silica (60.2%). (b) Residue content (wt%) after redeposition of samples on silver membrane filters. The reference line shows the non-silica content of the bulk material (approximately 40%). The MF treatment effectively removes the polyester resin, whereas using THF leads to an increase in residue. This increase is likely due to the formation of a swelling PVC-polyester network.

bulk dust samples. Independent samples t-tests revealed no statistically significant differences ($P = 0.05$ as the threshold) between THF and MF for Quartz, Cristobalite, or total silica percentages for all samples across different filter sizes (see Supplementary Table S.3).

Figure 3b shows the mass of post-treatment residue (excluding PVC residue) relative to PVC mass for various filter sizes. Gravimetric analysis determined the non-volatile residue from the resin binder and other non-silica components of the stone. The PVC residue in each spiked sample was calculated from the mean residue/ash content of blank PVC after processing with THF/MF (as shown in Table 2). This suggests that MF is a more effective method for removing PVC content. The mean residual percentage after the THF process (41.57%) was significantly higher than that of MF-treated samples (25.17%). A comparison of residue levels reveals differing behaviors between MF and THF as PVC mass changes. Theoretically, given polyester's poor compatibility with THF, the remaining residue mass should approximate the non-silica bulk content (40%). However, a statistically significant positive linear relationship exists between PVC Mass and Residue% (slope = 0.83, $P = 0.0066$). With increasing PVC mass, the residual amount shows a consistent upward trend, indicating a potential interaction between PVC and polyester in THF. In contrast, the MF process efficiently removes polyester resin through ashing, resulting in lower overall residue

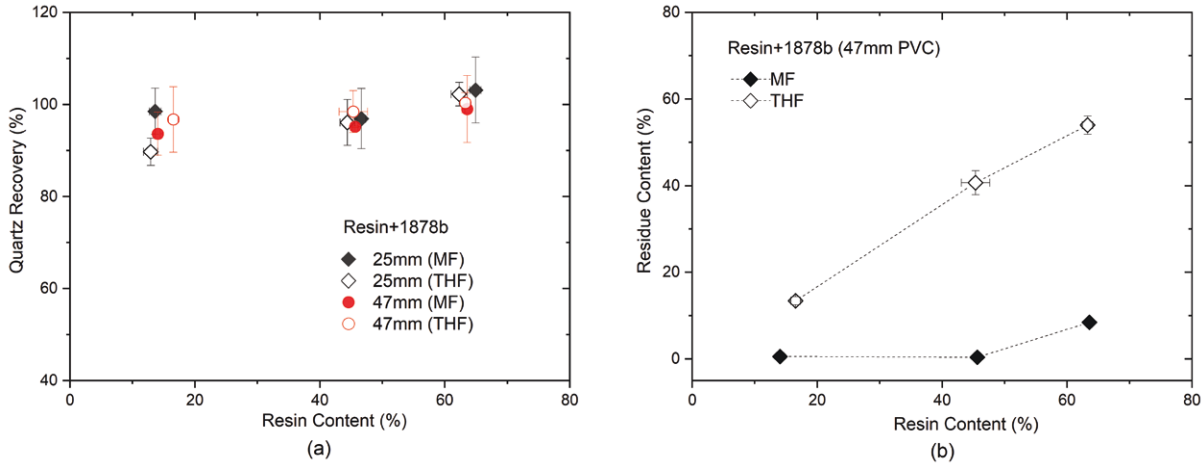

Fig. 4. Sanding dust from cured synthetic polyester resin blocks was mixed with approximately 500 µg of 1878b to create different resin compositions (16.7%, 50%, 66.7%). (a) The recovery rate of quartz was measured as a function of resin content for the spiked mixtures on 25 mm and 47 mm PVC, which were treated using either MF or THF. (b) The residue levels were measured after being redeposited onto silver membrane filters as a function of resin content in the tested mixture.

levels in the samples and remains nearly unchanged across the PVC mass.

Resin content and residue formation

Gravimetric analysis showed that Stone A samples treated with THF exhibited more non-volatile residue than those treated with MF. Spiked samples were prepared to quantify these residues and investigate their correlation with the stone's inherent resin content. These samples contained a known mass of SRM 1878b (about 500 µg) combined with varying quantities of laboratory-synthesized polyester resin dust, with a mass ratio of resin/SRM = 0.2, 1, and 2. Quartz recovery rates showed no substantial variation between MF-treated (99.6% ± 6.5%) and THF-treated (97.8% ± 6.0%) samples, as illustrated in Figure 4a. This consistency held regardless of the resin content and filter size used. The engineered stone dust simulant was created by manually combining cured resin sanding dust and pure silica powder. Unlike the actual engineered stone dust, the silica particles in this mixture are unbound and not embedded within the polymer structure. This unbound state likely prevents significant mass loss during polyester swelling in the presence of THF, potentially explaining the consistent TH and MF results for the Quartz recovery.

Analysis of 47 mm filters reveals distinct patterns in residue levels relative to the resin-to-SRM ratio for THF and MF processes (Fig. 4b). THF demonstrates a strong, nearly proportional (slope = 0.8701) positive correlation between Resin% and Residue%, suggesting it mainly dissolves PVC, leaving behind residue that closely mirrors the initial resin amount in the stone. In contrast, MF displays a much weaker correlation (slope = 0.1404) where Residue% stays low despite changes in Resin%. This indicates MF is more efficient at removing polyester resin, and its residue composition is less dependent on the initial resin content than THF. THF residue appears directly tied to the initial resin quantity with little proportional change. At the same time, MF leads to lower residue amounts that are not significantly affected by the starting resin percentage.

Potential interference mechanisms

The method of using THF to dissolve PVC filters for crystalline silica analysis relies on the assumption that the PVC will completely dissolve and the silica will remain inert, allowing for quantitative transfer and analysis. A pre-treatment step to remove the sample collection filter (eg PVC) and other interfering species, such as organic compounds, from the aerosol sample is crucial to improve measurement sensitivity and mitigate some potential interferences from the sample matrix. Therefore, the effectiveness of any pretreatment method hinges on its ability to isolate the target silica particles without altering them, allowing for a precise quantitative transfer and analysis. However, our study shows this process can be disrupted by interacting polymer components found in some engineered stones (eg Stone A). Although the cured polyester resin is crosslinked and cannot dissolve into free polymer chains, THF can diffuse into the polymer matrix if it finds compatible polarity. This causes the polymer to swell and soften, as solvent molecules occupy spaces between polymer chains. As a result, THF transforms hard resin dust particles into a gelatinous, swollen

state. Any portion of the resin not fully crosslinked (e.g. linear polymer fragments or uncured resin) may dissolve entirely into the THF. The remainder swells into a gel-like agglomerate. This swelling could physically trap silica particles inside the agglomerate, hindering their proper suspension and transfer onto the silver filter during redeposition. Another possibility is that partially dissolved or swollen resin components might precipitate or deposit on the silver filter along with the silica. This could coat the silica particles and weaken the X-ray signal or lead to mass loss during transfer if the residue is sticky.

Study limitations

The investigation focused on a limited number of engineered stone types (2 polyester-based, one acrylic-based, one laboratory-synthetic formulation). The results may not be generalizable to the full spectrum of engineered stone products available on the market, which exhibit wide variations in silica content, resin type, and additives. The study utilized laboratory-generated dust and direct filter loading, which may not accurately replicate the complex matrix and particle characteristics of workplace air samples. While the study investigated key hypotheses, other factors not examined could influence THF compatibility.

Addressing the analysis of previously collected samples and the development of a correction factor for potential underestimates presents significant challenges. Developing a reliable correction model is likely unfeasible for several reasons. First, considerable variability in RCS levels can exist from batch to batch, even within the same type of engineered stone product, making a universal correction difficult. Second, the underestimation of RCS when using THF is specific to certain polymeric resins and additives used in the stone's manufacturing. The level of uncertainty can also vary depending on the specific sampling and laboratory preparation procedures used, further complicating any attempt to retroactively correct data. Given these complexities, a more practical approach for future analyses is to be cautious when selecting a preparation method. It is suggested to prioritize non-chemical dissolution methods, such as muffle furnace ashing or low-temperature plasma ashing over THF dissolution when analyzing engineered stone samples known or suspected to contain interfering polyester resins.

Conclusions

There was a significant variability in crystalline silica content across different batches of Stone A, even when analyzed with the presumably more reliable muffle furnace method. This indicates that material heterogeneity is a significant factor contributing to measurement uncertainty in such laboratory evaluations. When analyzing samples from the same batch collected on 47 mm filters, the THF preparation method significantly underestimates the RCS content in Stone A, particularly with smaller sample sizes, compared to the MF ashing method. However, no significant differences are found between the MF and THF methods for samples prepared from Stone B, C, and laboratory-synthetic resin-silica mixture. This indicates that the particular composition and chemistry of the polymer binder, along with other organic additives within the stone, significantly influence the polymer-THF interaction, consequently affecting the THF process used for preparation. Using 47 mm filters with high PVC mass presented dissolution issues in THF. The incomplete dissolution of the filter may complicate the interaction with the swelling of the polyester matrix, making the THF method less reliable than MF for preparing samples for RCS measurement. Samples processed using the MF method exhibited consistently higher crystalline silica content than the THF method across all tested stone types and showed less sensitivity to the resin percentage within the stone. Additionally, MF ashing produced less residue after the treatment, suggesting its potential suitability for a broader variety of engineered stone products.

Our study suggests MF ashing as a preferred sample preparation method for respirable dust samples that may involve working with engineered stones. It is particularly critical when analyzing samples known or suspected to contain polyester resins, when the resin type is unknown, or when low dust loadings (<0.5 mg) are anticipated (especially when 47 mm PVC filters are desirable to use, for example, using certain samplers at higher sampling flowrate to lower the detection limit). This method can effectively remove the organic resin matrix, minimizing the potential for chemical interferences observed with THF. If THF dissolution must be used (eg due to equipment limitations), users need to exercise caution and visually confirm the dissolution of the PVC filter. They also need to be aware of residue levels and the high potential for underestimating RCS content in engineered stone samples. Using 25 mm or 37 mm sizes can help reduce complications related to incomplete dissolution of PVC and interactions with the swelling polymeric components in engineered stone. For sample treatment, further research can help reveal THF compatibility with a broader range of engineered stone products and other ashing techniques (eg LTA).

The current study identified potential underestimation of RCS in certain engineered stone products within a controlled laboratory environment. Field studies that

analyze air samples collected from facilities where various engineered stone slabs are processed simultaneously could provide additional insights into the influence of actual exposure scenarios.

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 (NIOSH), Centers for Disease Control and Prevention (CDC). The mention of any company or product does not constitute an endorsement by NIOSH/CDC.

Author contributions

Chen Wang: experiments and investigation, data collection, analysis, and interpretation, original draft preparation, writing, reviewing, and editing. Kabir Rishi: experiments and investigation, reviewing and editing. Bon Ki Ku: experiments and investigation, reviewing and editing. Pramod Kulkarni: project administration, writing, reviewing, and editing. Drew Thompson: experiments and investigation, reviewing and editing. Chaolong Qi: experiments and investigation, reviewing and editing.

Conflict of interest

The authors declare no conflicts of interest.

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Ethics approval

This activity was reviewed by CDC, deemed research not involving human subjects, and was conducted consistent with applicable federal law and CDC policy.

Data availability

The data generated or analyzed during this study can be found within the published article and its supplementary files. Additional data is available from the corresponding author on reasonable request.

Supplementary material

Supplementary material is available at *Annals of Work Exposures and Health* online.

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