



Application of End-of-Shift Respirable Crystalline Silica Monitoring to Construction

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Application of End-of-Shift Respirable Crystalline Silica Monitoring to Construction

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FINAL REPORT

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EXECUTIVE SUMMARY

A pilot project was conducted to determine the effect of common construction dusts as interferences in a new portable end-of-shift (EoS), direct-on-filter (DoF) sampling and analysis method for respirable crystalline silica (RCS), in this case quartz. The sampling and analysis system was developed by the Pittsburgh Mining Research Division of the National Institute for Occupational Safety and Health (NIOSH) for mineral dusts containing quartz in the mining environment. NIOSH provided training at their site for the investigators in this project. Construction dusts were prepared from plaster, drywall, cement and brick by grinding bulk materials to dust, aerosolizing the dust, and collecting the respirable fraction with high flow-rate respirable cyclones. Laboratory samples were generated by loading filters with different levels of commercial α -quartz powder (Min-u-Sil 5), and different levels of the interfering dusts, singly and in combination. Samples were analyzed by the EoS-DoF FTIR procedure and some samples then sent for confirmatory x-ray diffraction (XRD) analysis at Maxxam Laboratory.

Although the results of this study show promise for future research, this pilot project does not reach a comprehensive conclusion regarding the suitability of the DoF-EoS FTIR procedure for RCS in construction dust in part because of two unexpected issues which arose during this study. Both issues were investigated and are important considerations for any future study. First, the two Certified Reference Materials (CRMs) from the National Institute of Standards and Technology (NIST), 1878a and 1878b, appear to give different results when used to calibrate XRD analysis of Min-u-Sil 5. This issue will require careful future study and may lead to authoritative recommendations regarding the use of these CRMs by researchers and commercial analytical laboratories. Second, attempting to apply materials in sequence to a filter gave poor variance in results, and a procedure using a single mixture addition was able to give much tighter variance and results more consistent with expectations. Unfortunately, resources available under the project did not allow the XRD analysis of this second sample set, although the samples have been retained in case resources become available in the future.

The results from this second set of prepared samples and FTIR analyses were sent to NIOSH for statistical analysis. The results show that a) plaster and drywall dusts do not interfere substantially with the quartz measurement; b) cement does not interfere with the quartz measurement, but it does change the background absorbance of the filter; and c) in addition to having a substantial quartz content that has to be carefully evaluated in any study, brick dust may also contain an additional material, probably a silicate mineral, which interferes additionally with the quartz peak. In other words, the presence of cement leads to lower quartz values and brick leads to higher values.

Overall, 83% of the quartz contents predicted from the averaged calibration data agreed within 50% of the adjusted nominal loadings. This result is encouraging given the high levels of interfering dusts. Samples loaded with smaller amounts of all four dusts in combination gave even better results, with all nine results within 25% of the adjusted nominal loadings. Both cement and brick could be correctable interferences once the identity of the interference is revealed, in the same way that correction is made for interfering mineral dusts in mines, and this is one of the further investigations suggested by this study. It also is important to further investigate the extent of the difference in XRD results from using NIST 1878a or NIST 1878b as the XRD calibration standards. A manuscript detailing the experience and results, as well as recommendations for further work has been accepted for publication.

INTRODUCTION

Exposure to respirable crystalline silica (RCS) by inhalation can cause silicosis, lung cancer, other respiratory diseases, and kidney diseases. Silica, especially quartz, is a common constituent of materials used in construction including concrete, cement, bricks, aggregates, granite, slate and limestone. Exposure to RCS can occur during common construction tasks such as using masonry saws, grinders, drills, jackhammers and handheld powered chipping tools; operating vehicle-mounted drilling rigs; milling; operating crushing machines; and using heavy equipment for demolition or certain other tasks. The U.S.

Occupational Safety and Health Administration (OSHA) estimates about two million construction workers are exposed to RCS in over 600,000 workplaces.

Studies have reported excessive exposures associated with certain construction tasks. For example, exposures ranging as high as 100 times the National Institute for Occupational Safety and Health (NIOSH) recommended limit of 0.05 mg m^{-3} have been reported. In 2003, OSHA examined enforcement data for the years 1997 to 2002 and identified high rates of noncompliance with the OSHA RCS permissible exposure limit (PEL), particularly in construction, where 24% of samples were more than three times the PEL in effect at that time (OSHA, 2016). A more recent analysis of OSHA enforcement data from January 2003 to December 2009 showed some improvement – only 19% of samples were more than three times the PEL—but still just 75% of samples complied with the PEL in effect at this time (OSHA, 2016).

Surveillance systems currently capture approximately 200 silicosis-related deaths annually among construction workers, with an unknown number going unreported or undiagnosed. Findings for the years 1990-1999 indicate that the construction industry was the industrial sector most frequently recorded on death certificates documenting deaths related to silicosis (13.4% of the total). More recent SENSOR data through 2002 indicated that construction exposures in specific states (Michigan, New Jersey, and Ohio) averaged 9.2% of all silicosis deaths, and 14.2% in California. As part of a new comprehensive standard for silica in construction in effect from September 23rd, 2017, alongside a similar rule for General Industry taking effect in 2018, OSHA lowered their PEL for RCS to 0.05 mg m^{-3} RCS (all forms) and added a concentration level where exceedances would drive further enforcement actions (action level; concentrations higher than 0.025 mg m^{-3}). OSHA estimates that more than 840,000 construction workers are exposed to RCS levels that exceed the new PEL. OSHA's Preliminary Economic Analysis and Initial Regulatory Flexibility Analysis expects a net benefit between \$2.8 and 4.7 billion annually over the next 60 years by preventing between 579 and 796 fatalities from RCS exposure in all industries.

Compliance with exposure limits requires the collection of respirable dust to determine an individual's exposure to RCS. A key tool, used to assess the exposure of workers to hazardous dusts and the effectiveness of controls, is to obtain personal samples of dust over a specific period of work and then to measure for the mass of a hazardous substance. Respirable dust is sampled from air using a cyclone or impactor to separate the respirable fraction from aerosol. Evaluation of RCS uses off-site sophisticated laboratory analysis, but this can involve results being returned up to several weeks following the period sampled. Long lag times can lead to unacceptable conditions persisting during the interim without being recognized or addressed.

A methodology to quickly determine monitoring exposure results, even if the accuracy is outside of that required for compliance purposes, can be vitally important. NIOSH has developed a field-ready instrument capable of an end-of-shift (EoS) measurement for RCS contained in airborne dusts in the mining sector (Cauda et al., 2016; Hart et al., 2018). RCS is collected on a direct-on-filter (DoF) sampler and then analyzed in an on-site field-portable FTIR spectrometers. Since FTIR is a non-destructive analysis, samples can still be submitted to a laboratory for further analysis.

This method promises to be applicable to monitoring RCS in the construction sector. However, the construction samples contain not only silica but other components, which are typically different from those found in mines and quarries. The presence of such components may interfere with the FTIR response from RCS in a manner which may require corrections to be applied to obtain a valid result. The goal of this study is to evaluate possible interferences from different types of construction dusts—including drywall, plaster, cement, and brick—in laboratory-generated mixed dust samples.

METHOD

Respirable dust collection and characterization

A commercial quartz powder (Min-U-Sil 5, US Silica Company, Berkeley Springs, West Virginia) is a finely ground quartz (99.2% silica) which was used as the reference standard in this work. It has been well characterized; its size range (> 95% less than 5, median 1.6, μm physical diameter) is in the appropriate size range for respirable samples and its x-ray diffraction (XRD) response is similar to the National Institute for Science and Technology (NIST) Standard 1878a (Verma and Shaw, 2001), which was too expensive to be used in this project.

Since respirable dusts of plaster, cement, drywall, and brick are not commercially available, typical raw materials were obtained from a commercial hardware store: plaster (Plaster of Paris #10313, DAP Products, Baltimore), drywall (Liflite, Continental Building Products, Herndon, Virginia), cement (Portland Cement Type I/II # 1124, Quikrete, Atlanta), and brick (smooth red common core, Plant #25 Brickhaven, General Shale, Johnson City, Tennessee). These products typically are manufactured to ASTM Standards; however, that does not preclude a brand-to-brand or lot-to-lot variation in composition. In this pilot project, it was only possible to evaluate one sample of each product type. The cement and plaster were mixed with water in accordance with manufacturer's instructions and allowed to set before use. All four materials were then ground into fine powders. Because the powders could not be directly resuspended due to their tendency to aggregate, a blender (shown in Figure 1) was applied to break aggregates into small particles and to aerosolize these small particles. Then, a high-flow cyclone was placed inside the blending jar and operated at around 10 Lpm to sample the respirable fraction of the dust particles. Although this cyclone has been tested for performance with respect to the ISO respirable sampling convention in one laboratory, publication of those results is awaiting confirmation by a second laboratory. Table 1 shows that brick had the highest production rate while drywall had the lowest. In total, 400 mg of each type of dust was collected.

Figure 1. Experimental setup for respirable plaster dust collection. Note respirable cyclone was immersed inside the blender.

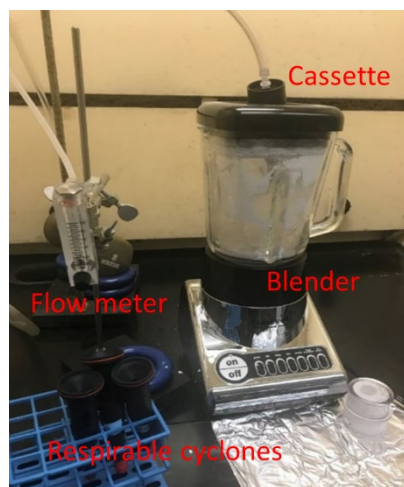


Table 1. Hourly collection rate of respirable dust by the respirable cyclone

Unit: mg/hr	Plaster	Cement	Drywall	Brick
Mean	30.13	45.55	7.61	80.65
Standard deviation	6.51	15.81	3.60	27.85

Splits of the bulk dust samples were sent to an external commercial laboratory for bulk XRD analysis. Drywall and plaster had no detectable quartz (reporting limit = 0.25% by weight), while cement contained 0.34% by weight and brick 12% by weight. The quartz content of brick was taken into account in the methods and in calculations of the results. However, a quartz content of 8% in the brick dust may give more consistent results with what was observed by FTIR.

Sampling cassettes

Sampling cassettes for the EoS silica method by Fourier-transform infra-red spectroscopy (FTIR) have been proposed previously (Cauda, et al., 2016). The cassettes used in this study consist of a 37 mm four-piece (bottom (outlet), two center rings in the middle, and top) conductive polypropylene cassette, containing, in order from the bottom, a wheel-shaped aluminum support without a center to allow transmission of infra-red radiation, a 5 μm pore-size PVC filter and a cellulose separator ring between the two center ring pieces. The cassettes are specially made for this method (745PVC-CF-FTIR, Zefon International, Inc., Ocala, FL) and are intended in field use to be fit onto a cyclone, with either the top inlet piece in place to fit on a Dorr-Oliver nylon cyclone, or with the inlet piece removed to fit on most other cyclones. In this pilot project, no air samples were collected. All experimental spikes were prepared by pipetting suspended particulate directly onto the collection filter.

Slurry deposition

Controlling airborne dust deposition onto a filter to obtain a specific loading of dust is challenging. Instead, assuming particles are well mixed as suspension, filtration of slurry is typically used to achieve the same goal of dust collection. The procedure in OSHA (1981, rev. 2016) Method ID-142 was followed. The suspension was prepared with a ratio of 1 mg particles to 1 mL 2-propanol. The suspension was put in a sonication bath where the ultrasound energy traveled through the water to disperse particles. The cassettes were prepared with a cellulose support pad (Zefon International, FSP37) at bottom, a PVC filter (Zefon International, FPVC537), and a cellulose support ring (Zefon International, FSP37R) on top to guarantee an airtight seal.

Four different levels of quartz slurry – 0, 25, 50 and 100 μg (blank, low, medium and high, respectively) – were added to each of two levels, 500 and 1000 μg , of each of the four dusts, separately. A typical 4-hour air sample through a standard cyclone operating around 2 Lmin^{-1} represents approximately 0.5 cubic meter of air, so the loadings selected represent concentrations of approximately 1 and 2 mgm^{-3} and are thus comparable to the ACGIH TLV of 3 mgm^{-3} for respirable dust. This was done in triplicate for a total of 96 samples. In addition, triplicate sets were made of samples containing 50 μg quartz and 25 μg of each dust combined, 50 μg quartz and 50 μg of each dust combined, 50 μg quartz and 100 μg of each dust combined, and 50 μg quartz and 250 μg of each dust combined (12 samples in total). Finally, triplicate sets of calibration samples (0, 25, 50, and 100 μg quartz without interference) were prepared for an overall total of 120 samples. See table 2 for summary.

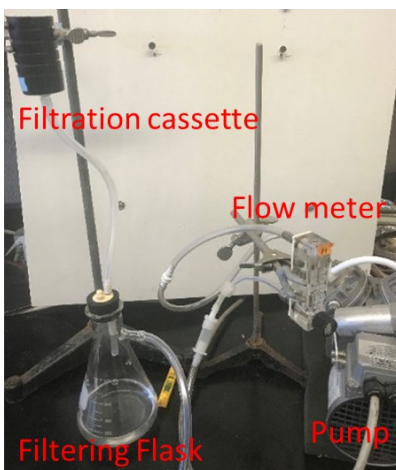
Table 2. Summary of samples of quartz plus interference.

Interference	Quantity (µg)	Amount of quartz (µg); 3 samples each			
Plaster	500	0	25	50	100
	1000	0	25	50	100
Drywall	500	0	25	50	100
	1000	0	25	50	100
Cement	500	0	25	50	100
	1000	0	25	50	100
Brick	500	0	25	50	100
	1000	0	25	50	100
PDCB (plaster, drywall, cement and brick)	25 of each			50	
	50 of each			50	
	100 of each			50	
	250 of each			50	

Two protocols were applied separately for dispensing slurry on filter. The first protocol, *sequential addition*, involved 2 mL of 2-propanol pipetted onto the filter so that the filter was wetted to enhance even distribution. The quartz suspension and construction dust slurry were then pipetted in sequence and immediately vacuumed for approximately 10 seconds. This protocol was used for all samples where a single interference was added after the quartz. However, when interferences were added one after the other, there was clearly a tendency for the quartz to be washed to the edge of the filter, leading to low results, as the quartz was moved away from the IR beam. Thus, a second protocol, *mixed addition*, was applied to a second set of all mixed samples other than those with quartz alone. Two mL of 2-propanol were pipetted into a test tube, followed by the quartz and construction dust suspension, and then placed into a sonication bath. Mixing the 2-propanol and suspensions in a test tube helped to evenly distribute the suspension across the filter and prevented particles from layering and masking other particles. The test tube was taken out of the sonication bath, shaken by hand, and gently poured into the cassette to avoid splashing on the cassette walls, so the entirety of the content was on the filter.

Vacuuming helped clear the 2-propanol from the system while trapping the particles in the suspension onto the filter. The filters were left overnight to dry so that any remaining 2-propanol would evaporate and not hinder with FTIR analysis. The support pad was then removed and replaced with a metal wheel because the thick pad could interfere with FTIR measurements.

Figure 2. Experimental setup for slurry deposition



Determination of quartz by FTIR

This determination of quartz by FTIR spectroscopy is a direct on-filter (DoF) analysis method and so there is no need to remove filters from the sampling cassette. Cassettes are conveniently and directly mounted on a special holder in a portable FTIR spectrometer (Thermo-Nicolet iS5). The infra-red beam passes through the center of the front end of the cassette, the sample and the filter and is detected at the rear end. Before the cassettes were analyzed, the background was recorded by running an unused filter. The blank filter was re-analyzed every 20 samples. This cancelled out any contribution from the filter itself and moisture in the system. After measurement, data were subjected to discriminant analysis using TQ Analyst EZ Edition software (Thermo Fisher Scientific Inc, USA) for the wave ranges between $767 - 816 \text{ cm}^{-1}$ to obtain absorption area for crystalline silica. FTIR calibration was attempted using the average spectra from triplicate quartz spikes nominally at 25, 50 and 100 μg . However, the specific lot of filters used for this test were different from the lot of the filter used to “zero” the instrument, leading to a problem with the analysis. A further calibration set (3 samples each at 0, 25, 50, and 100 μg quartz) were prepared using a “zero” blank filter from the same lot and analyzed twice to document operator variability. One outlier result was excluded from the analysis.

Determination of silica by XRD

Samples were prepared and analyzed at the same contract laboratory used by NIOSH (Bureau Veritas North America, now Maxxam). For the bulk samples, approximately 2 mg of neat sample was weighed into a 15-mL test tube. Approximately 10 mL of 2-propanol was added into the test tube to create a suspension. The test tube was placed in an ultrasonic bath for about 15 minutes until agglomerated particles were broken up. The sample suspension was vortexed and immediately re-deposited onto a 25-mm diameter silver membrane filter. First, a silver membrane filter was placed in the vacuum filtration unit. Next, approximately 2 mL of 2-propanol was added into the filtration funnel, followed by the sample suspension and test tube rinses. Finally, vacuum was applied to deposit the suspension onto the filter. The silver membrane filter was transferred to a sample plate and placed in the automated sample changer for analysis by XRD.

Filter samples were analyzed according to NIOSH Method 7500 (NMAM 4th Edition). The filter was removed from the cassette and folded two times into a quarter pie-shaped pocket to contain the particulate inside. A drop of 2-propanol was added to the inside of the cassette lid and the back side of the sample

filter was used to wipe the interior of the sampling cassette. (Note: this is not a necessary procedure for these samples, but it is the laboratory standard operating procedure for air samples.) The filter was transferred to a 15-mL sample vial. The filter was dissolved by the addition of 6 mL of tetrahydrofuran (THF) to the sample vial. The sample was mixed by vortex. The sample vial was covered with aluminum foil and placed in an ultrasonic bath for fifteen minutes.

The sample suspension was then transferred to a silver-membrane filter. First, a silver-membrane filter was placed in the vacuum filtration unit. Next, approximately 2 mL of THF solvent was placed onto the filter. The sample suspension was vortexed and immediately added onto the silver membrane filter. The sample vial was rinsed with three separate portions of THF. Each rinse was added to the sample on top of the silver membrane filter. Finally, vacuum was applied to deposit the sample suspension onto the filter. The silver-membrane filter was transferred to a sample plate and placed in the automated sample changer for analysis by XRD.

Analysis was carried out on a Bruker D8 Endeavor X-ray diffractometer with automated sample changer, with the following set-up: Cu target: 40 kV, 40 mA; scan speed: 0.2 seconds/step; scan axis: theta/theta; sampling width: 0.010 degree; detector: LYNXEYE_XE_T, continuous PSD fast mode, 4.1 degree PSD opening; slit: 2.5 degree primary and secondary axial Soller mounts; divergence slit: fixed sample illumination, 8 mm; anti-scatter screen: automatic; rotation: 60 RPM phi stage. Calibration standards of alpha-quartz were prepared from NIST standard reference material 1878b. One media blank was prepared and analyzed with each sample run. Quartz was not detected in the blanks. One pair of laboratory control samples were prepared and analyzed with each sample run. The spiked sample recoveries for quartz were within the statistical limits and the relative percent difference results for duplicates were within statistical limits.

RESULTS AND DISCUSSION

FTIR spectrum for quartz, plaster, drywall, cement, and brick

There are three IR absorption bands which can characterize SiO₂: As noted by Hlavay et al. (1978) the signals at 1079-1088 cm⁻¹ are attributed to asymmetric vibrations of (Si-O-Si); the signals at 804-805 cm⁻¹ are attributed to symmetric stretching vibrations of (Si-O-Si); and the signals at 459-463 cm⁻¹ are attributed to the bending vibration of (Si-O-Si). The quartz spectrum of interest in this study was limited within the wavenumber between 767 and 816 cm⁻¹, per Miller et al. (2012); an example spectrum of quartz samples is shown in Figure 3. The two peaks are unique for quartz while amorphous silica lacks such peaks.

Hemihydrate calcium sulfate (2CaSO₄·H₂O) is commonly found in plaster, while calcium sulfate dihydrate (CaSO₄·2H₂O) is commonly found in drywall. These chemicals are similar and thus plaster and drywall have characteristic IR absorption bands (Hlavay et al., 1978), as shown in Figure 4, at 1140 – 1080 cm⁻¹ and 600-680 cm⁻¹, resulting respectively from asymmetric SO₄²⁻ stretching and SO₄²⁻ bending (symmetric and antisymmetric). Cement has a different spectrum from those of drywall or plaster, and as noted by Derrick et al. (1999), shares the same peak of CO₃²⁻ stretching (1490 – 1370 cm⁻¹) as limestone or chalk (CaCO₃). Brick has a significant absorption band 1100 – 1000 cm⁻¹, which refers to asymmetric Si-O-Si stretching bend that is also found in Kaolin (Hlavay et al., 1999). Note that brick contains a significant level of quartz and peaks at both 800 and 780 cm⁻¹ were found in our samples. In summary, the target quartz absorption spectrum does not overlap with the construction dust spectra except for brick samples, where quartz is known to be present.

Figure 3. IR spectra for quartz

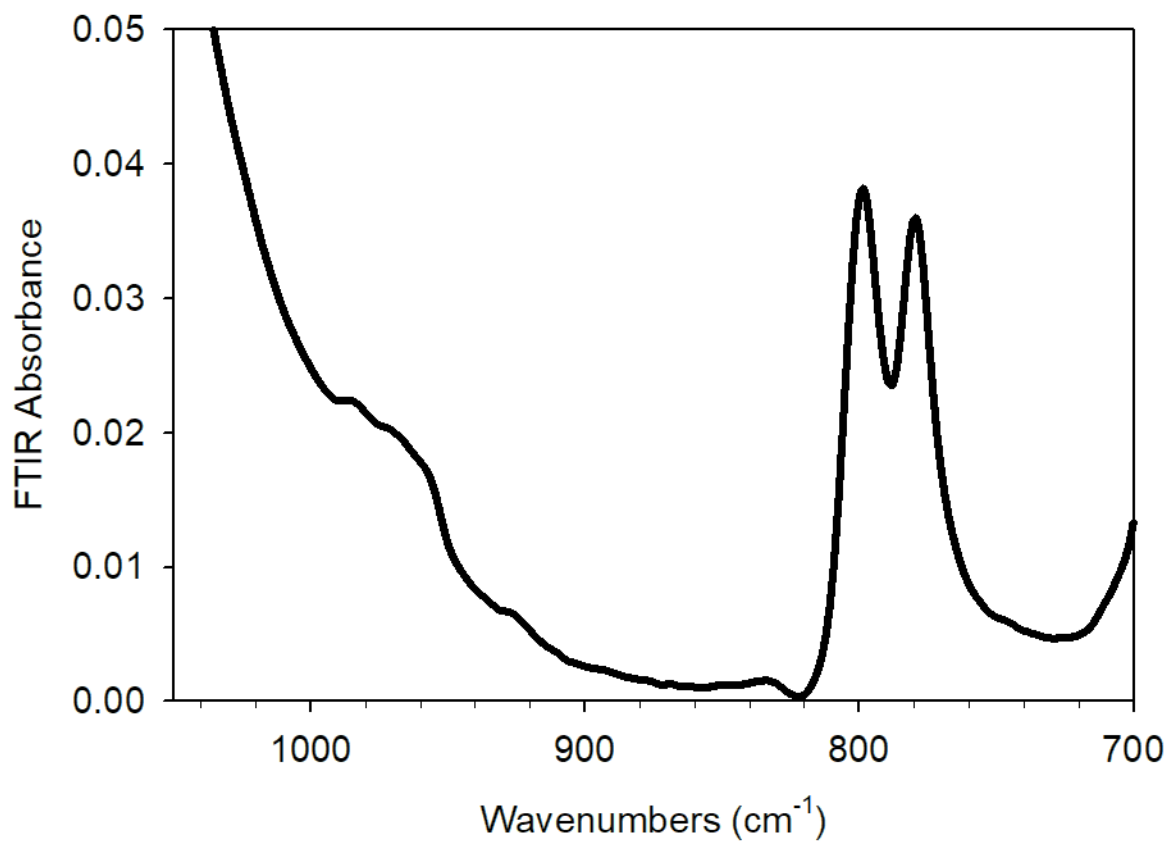
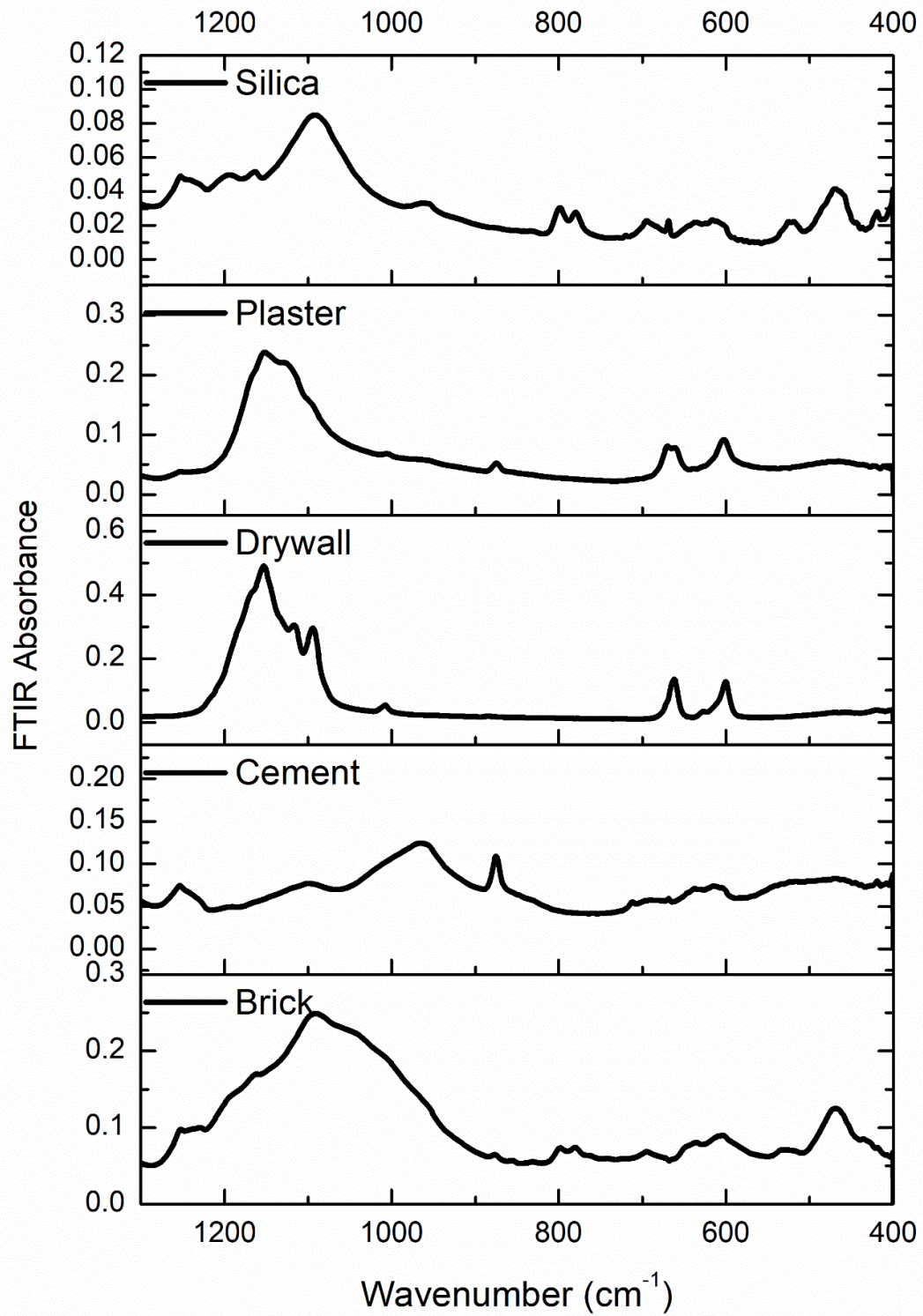


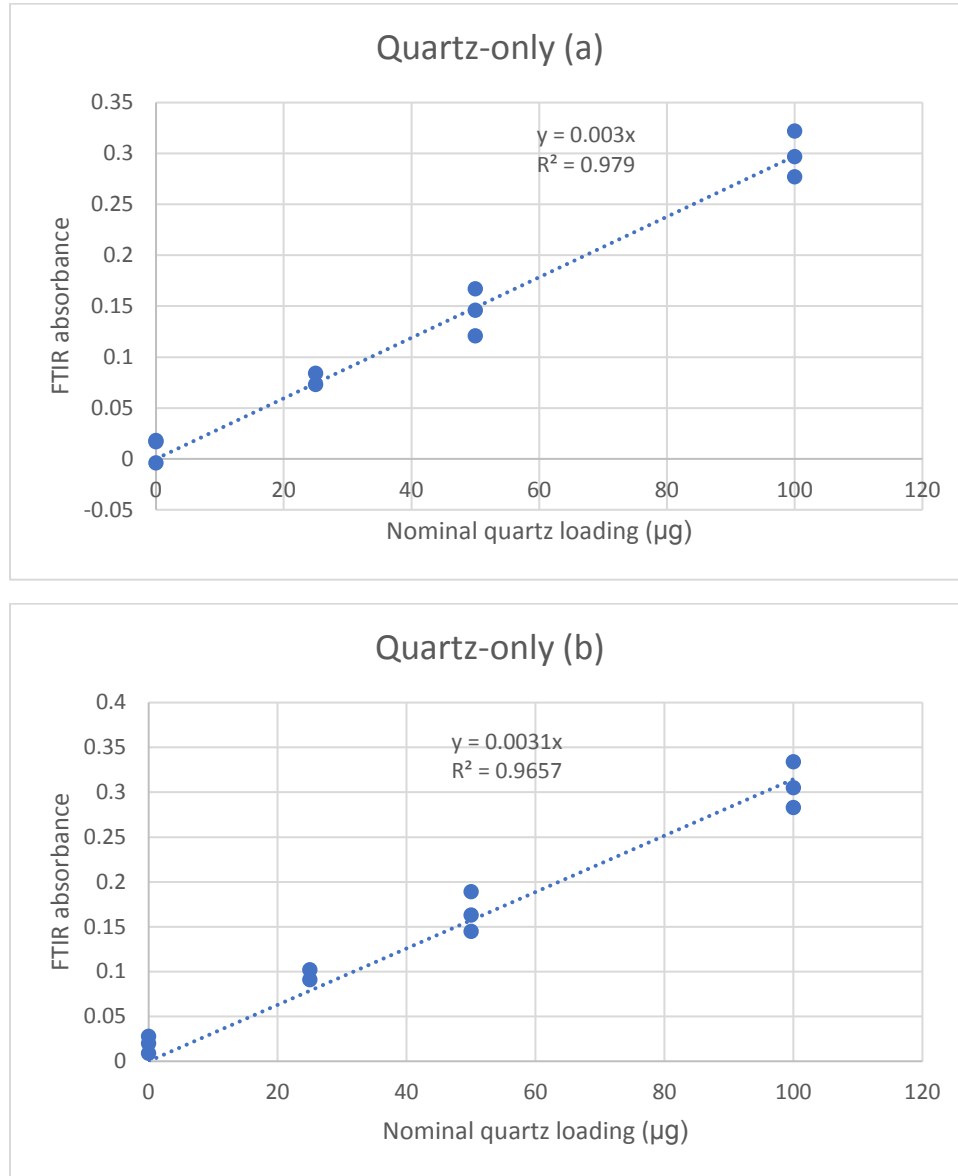
Figure 4. IR spectrum for quartz, plaster, drywall, cement, and brick, from top to bottom



Calibration from quartz slurry spikes

The second set of calibration samples gave a good correlation (minus one outlier from poor standard preparation), which gave practically identical results on re-analysis, as shown in Figure 5.

Figure 5. Set of quartz-only calibration samples analyzed twice by FTIR (a and b).



When the first set of samples were analyzed by XRD for confirmation purposes, the results were lower than expected, and a further set were made and split between the principle analytical laboratory and two other laboratories also accredited for NIOSH Method 7500⁽⁶⁾ analyses by AIHA. The results are given in the table 3.

Table 3: analysis of calibration standards at different laboratories

Nominal value	Original calibration set – primary lab	Round Robin set – primary lab	Round Robin set – alternative lab 1	Round Robin set – alternative lab 2	Average of both alternative lab results
25	20; 19; 19	16; 21	26; 28	23; 25	26
50	38; 37; 39	38; 37	50; 56	44; 49	50
100	80; 81; 89	85; 80	111; 111	91; 92	101

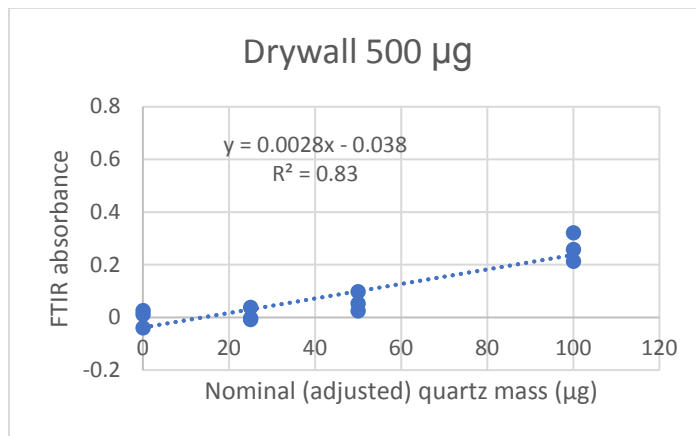
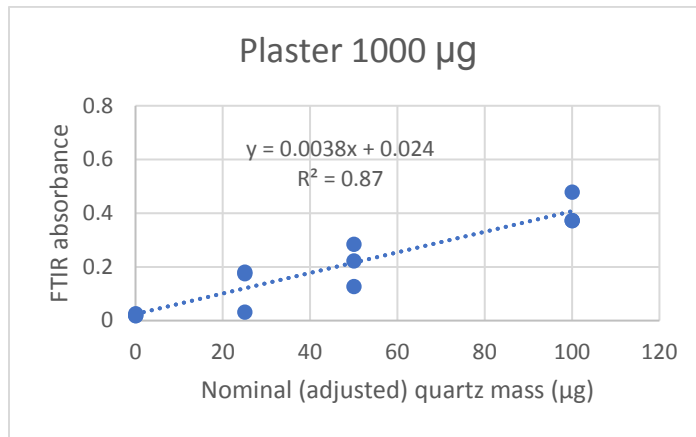
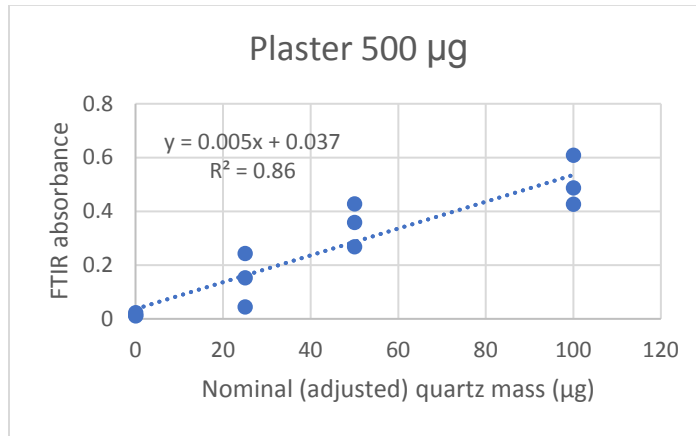
Both alternative laboratories used NIST 1878a as a calibration standard (alternative lab 2 used NIST 1878a directly, while alternative lab 1 used the filter Certified Reference Materials which were derived from NIST 1878a) while as noted in the procedure above the primary laboratory used NIST 1878b as their calibration standard. NIST 1878a resembles Min-u-Sil 5 more closely than does NIST 1878b and so the average XRD results from the alternative laboratories are close to the nominal values, thus not suggesting a bias from the spiking procedure. Comparing the entire data set in terms of nominal spike quantity (adjusted for quartz in the interference dust) against primary laboratory XRD result gives an offset of 18% (mean and median). Although the literature (Verma and Shaw, 2001; Dean and Page, 2006; Stacey, et al., 2009) does not suggest the difference in results from using 1878b as the calibration standard should be as great as that found here, the primary laboratory has notified the authors that they have previously seen differences in results of this magnitude. The nominal spike values are used in data examination.

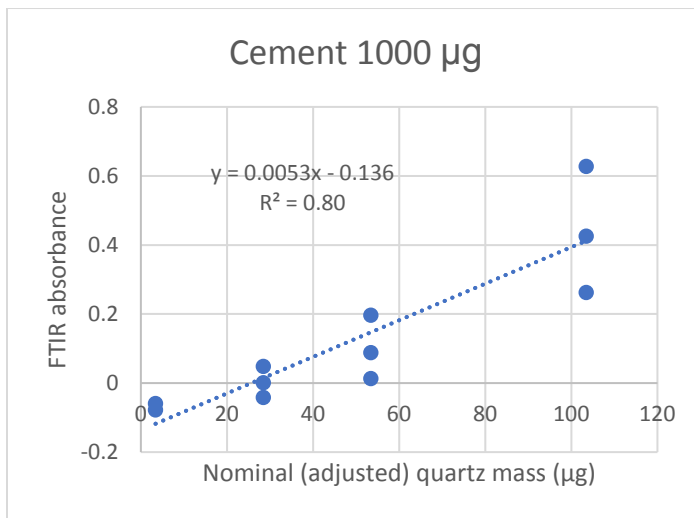
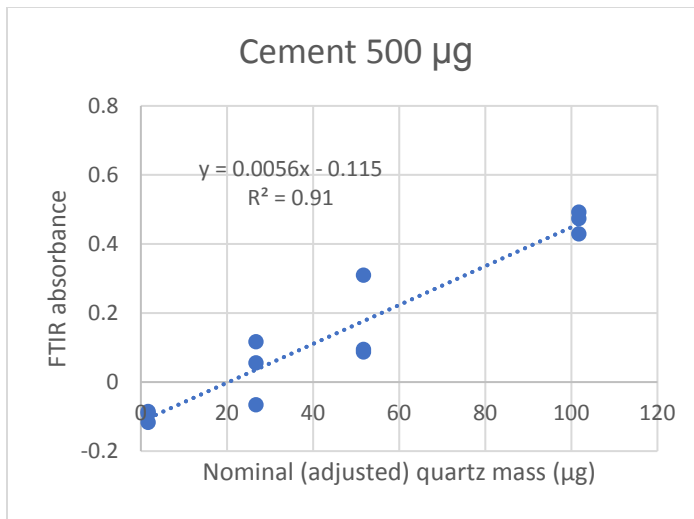
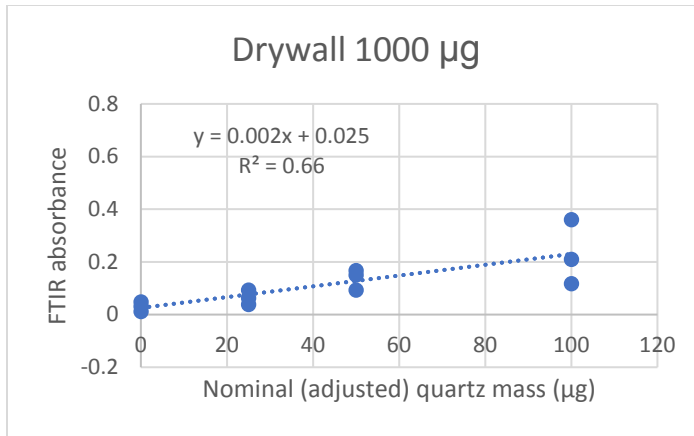
The effects of construction dust on quartz measurement (sequential spiking procedure)

Graphs of the nominal quartz quantity (adjusted for quartz in the interference dust) against FTIR absorbance reveal effects which differ by interference. The graphs are presented as figure 6. One extremely low value for 0 μg quartz was removed from Cement 1000 μg .

The plaster results show a good correlation between quartz mass and FTIR response with a practically zero intercept. The slope of the correlation is lower with larger plaster loading, which could indicate a degree of interference in the quartz signal (but this was not confirmed with the mixed addition procedure samples). Examination of the plaster absorbance in figure 4 shows a response above baseline in the quartz absorption region. The drywall results are like those from plaster, except that a smaller difference between slopes for the different quantities is commensurate with a lower baseline in the quartz absorbance region. However, the slopes for both quantities are lower than those for plaster, and the reason for this was not determined. The cement results are also similar to the plaster except that there is a large negative intercept, which becomes more negative with increasing cement content, in keeping with a negative dip in absorption that can be found in the quartz region. The slopes are similar suggesting that the quartz is otherwise being detected well. Finally, the brick results make it appear that the large quantity of quartz already present in the brick is overloading the detector. Summary results are in Table 4. These results, however, are not useful and have not been submitted for publication for reasons explained below.

Figure 6. FTIR absorbance vs. nominal spiked quartz amount (adjusted for quartz present in the interfering dust). First set of prepared sample: sequential addition.





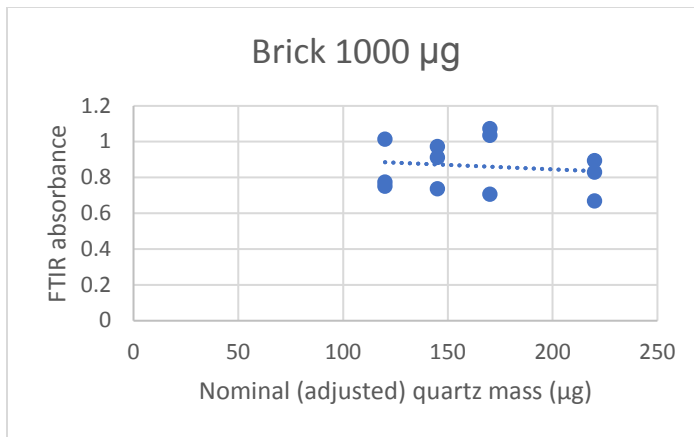
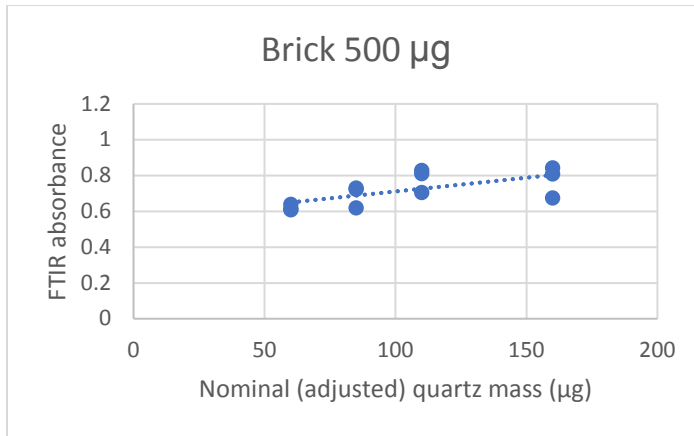


Table 4: Tentative relationship between FTIR quartz calibration and nominal dosing.
Note this relationship is tentative because a) the sequential dosing procedure led to poor results (see below for further explanation) and b) the FTIR calibration was on a possibly different lot of filters than the sample filters.

Interference	Quantity (μg)	Nominal (adjusted) quartz mass (μg)	Average Quartz mass by FTIR (n=3) (μg)	Cement adjusted for -ve intercept (+ 20 μg)
Plaster	500	0	3	
		25	29	
		50	69	
		100	99	
	1000	0	4	
		25	25	
		50	42	
		100	80	
Drywall	500	0	0	
		25	1	
		50	11	
		100	52	
	1000	0	6	
		25	12	
		50	27	
		100	45	
Cement	500	1.7	-19	1
		26.7	7	27
		51.7	32	52
		101.7	91	111
	1000	3.4	-14	6
		28.4	0	20
		53.4	20	40
		103.4	86	106
Brick	500	60	121	
		85	135	
		110	153	
		160	152	
	1000	120	166	
		145	172	
		170	184	
		220	156	
All four (PDCB)	25	53.1	37.5 (N=2)	
	50	56.2	67	
	100	62.3	72	
	250	80.9	63	

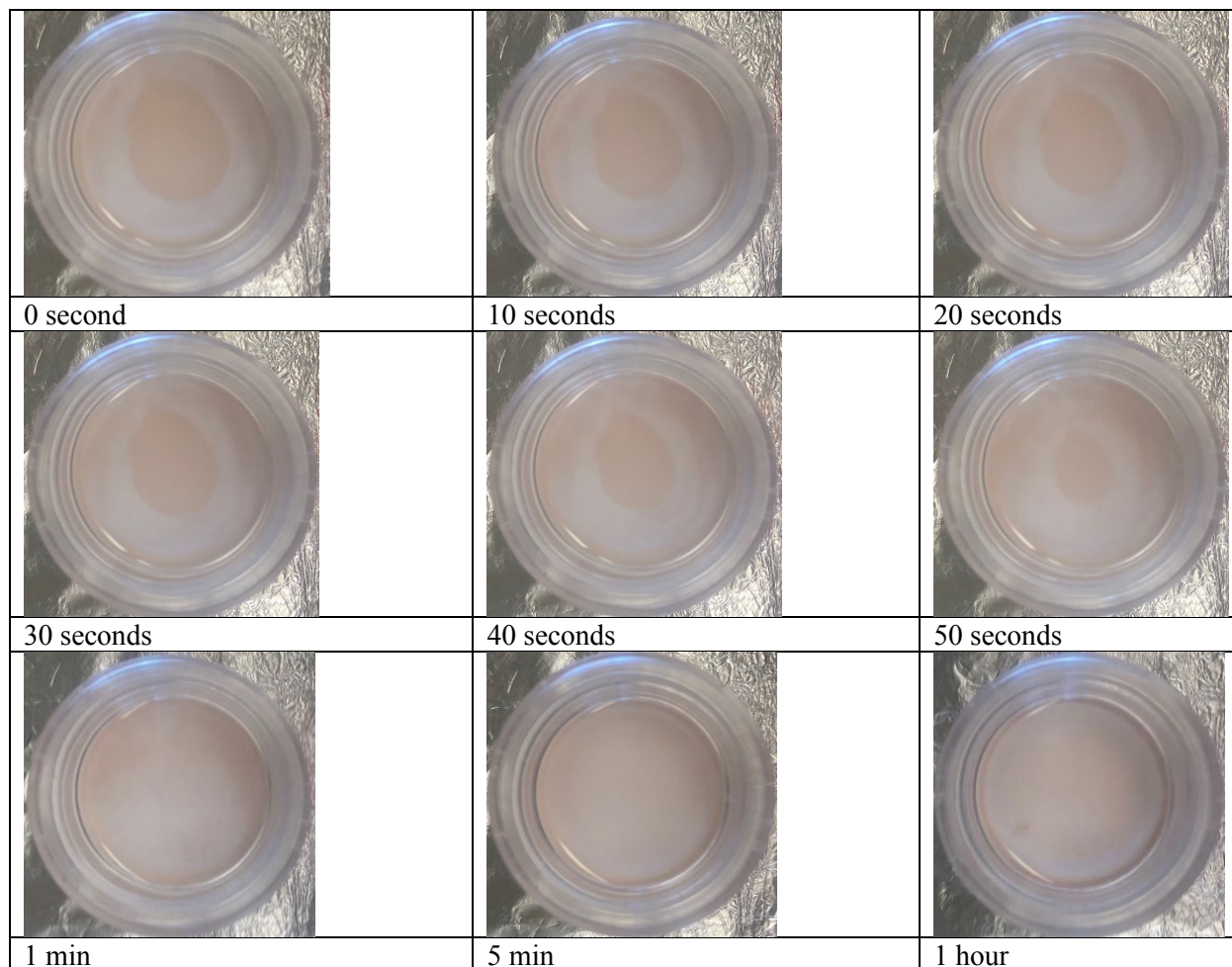
An issue of uneven deposition of the slurry

Figure 7 shows an uneven distribution of slurry. The effect was more pronounced when low-viscosity 2-propanol was applied. The first picture in Figure 7 demonstrates the brick particles occupied the filter center after brick slurry was pipetted. The flush mechanism implies the construction slurry occupied the filter center. It is possible that the repeated pipetting of the separate construction dust slurries may have pushed the previously deposited quartz slurry to the edges, perhaps providing anomalously low results. This might be responsible for the negative bias of FTIR measurement when the filter center was the detection zone. Second, pipetting in sequence (e.g. 2-propanol alone, then quartz slurry followed by brick slurry) requires time to mix. Figure 8 illustrates that brick suspension did not immediately mix with the first IPA. Rather, brick particles gradually diffused to pure 2-propanol and it took at least 1 minute to ‘evenly’ distribute on the filter from naked eyes. Since the slurry was vacuumed within 30 seconds during the experiment following the NIOSH Method protocol, this implies that 2-propanol, quartz slurry, and brick slurry were not yet well mixed before vacuuming, resulting in uneven deposition on the filter.

Figure 7. The comparison of brick slurry deposition pattern. Uneven distribution due to sequential addition (left) and even distribution using mixed addition (right).



Figure 8. The evolution of brick dust distribution in slurry over time with “pipette in sequence”



Measurement improvement by new mixed addition protocol

A new experimental protocol of “mixed addition” was proposed to replace the protocol of “sequential addition”. When this was done, even brick gave results with lower variance. Unfortunately, insufficient resources were available to also have these samples analyzed by XRD. Figure 9a-c shows the correlation coefficients have dramatically increased (after removal of two drywall 500 μg and one cement 1000 μg results, which were outliers of more than 3 standard deviations from the regression line without them). Figure 8 also shows that the absorption for quartz with plaster, cement, and drywall give similar responses (slopes between 0.003x and 0.0036x). These correlations were not forced through zero to explore whether there was an effect on intercept. A negative depression in absorbance from cement is visible. It may be the result of calcite in the cement, an observation consistent with proficiency test samples (Harper et al., 2014) and mine sample results (Emanuele Cauda, NIOSH – personal communication, January 2020). Note that the intercept is reduced more with 1000 μg cement dust compared to 500 μg . A smaller negative intercept is also visible in the drywall data; the value is smaller so any difference between the two loadings of drywall may be lost in the analytical variability. Figure 10 shows the brick samples, while Figure 11 shows the same results forced through the origin of the graph. Notice that the slope without forcing through the origin is much steeper than with the other interferences, but there is closer alignment with other interference figures

when the intercept is forced through the origin of the graph. Slopes, intercepts and correlation coefficients are given in Table 5.

Table 5. Slopes, intercepts and correlation coefficients of regression lines in figures 9-11.

	Regression slope	Intercept	Correlation coefficient (R ²)
Plaster 500 µg	0.0034x	0.134	0.996
Plaster 1000 µg	0.0034x	0.006	0.993
Drywall 500 µg	0.0035x	0.026	0.984
Drywall 1000 µg	0.0036x	0.020	0.991
Cement 500 µg	0.0030x	0.051	0.984
Cement 1000 µg	0.0032x	0.090	0.992
Brick 500 µg	0.0043x	0.127	0.984
Brick 1000 µg	0.0050x	0.200	0.987
Brick forced through origin 500 µg	0.0032x	0.000	0.913
Brick forced through origin 1000 µg	0.0038x	0.000	0.931

Figure 9 (a-c). The effect of construction dust (plaster, drywall and cement) on quartz FTIR measurement with the “mixed addition” protocol. Adjusted masses account for quartz in the matrix.

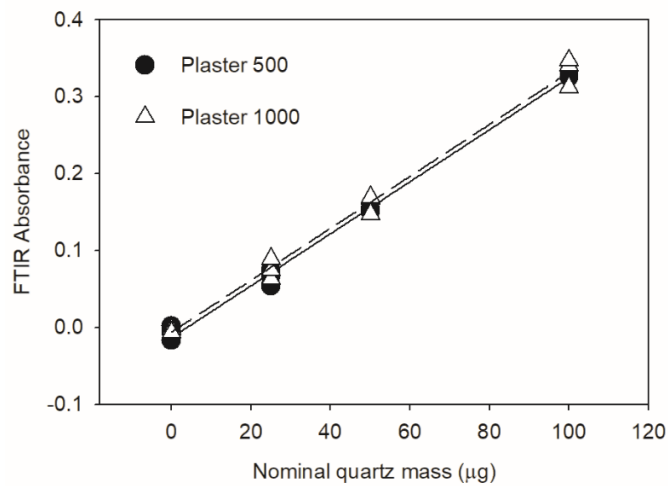
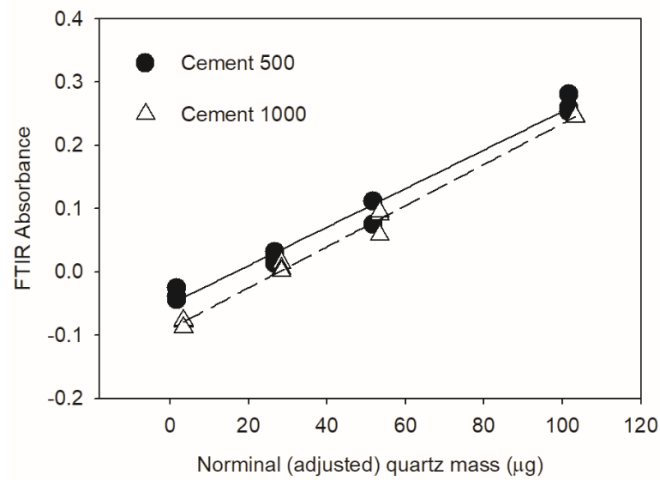
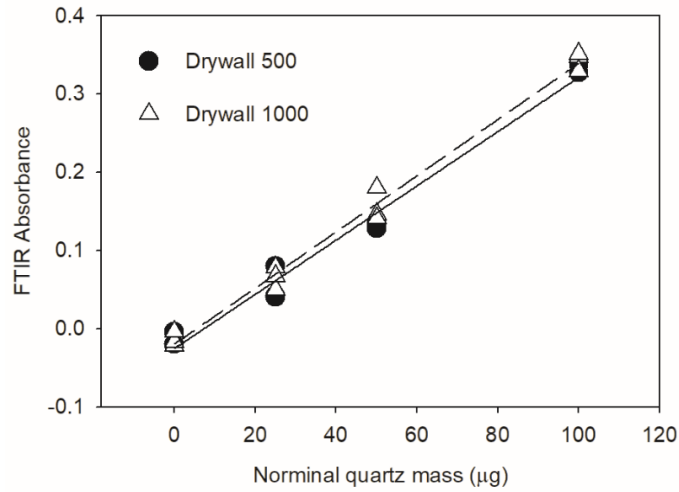


Figure 10. The effect of brick without forcing the regression through zero

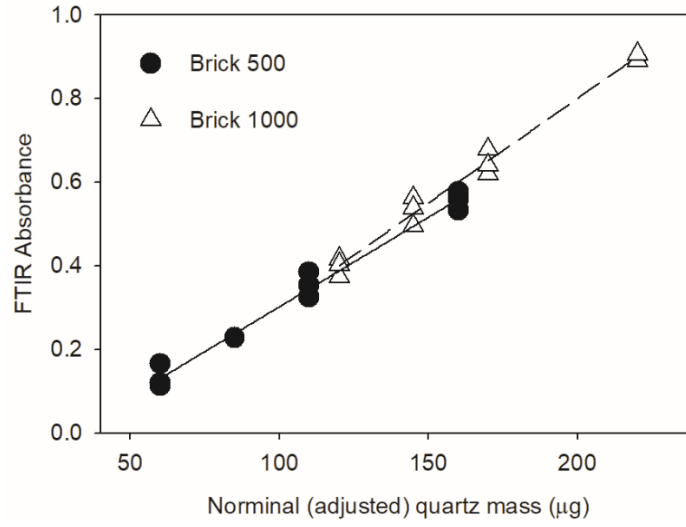
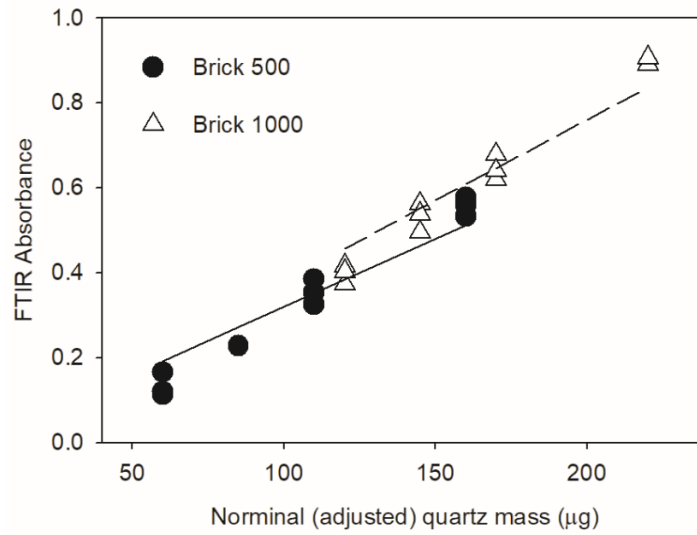


Figure 11. The effect of brick with forcing the regression through zero



The brick results may be affected by an inaccurate assessment of the quartz content of brick. In figures 10 and 11 the 12% quartz content from bulk XRD analysis was assumed, but the regression lines forced through zero or not become almost identical if the background is set at 8% instead. Nevertheless, the slopes are still steeper than those of quartz alone, or quartz in combination with plaster, drywall or cement. For brick 500 μg the slope is 0.0043 x while for brick 1000 μg it is 0.005 x, indicating there might be an interference from another component of brick, such as alumina or a clay mineral.

ANALYSIS OF THE DATA

To make conclusions about the mixed addition method, only those values between 20 and 110 μg quartz bracketing the target concentration (OSHA PEL of 50 μg in a 1 m^3 sample) were considered. No corrections were made for any interference effect other than accounting for quartz background in the interference. For brick, 8% was assumed, as noted above. Note that if 12% quartz content is assumed instead for brick, all the values for brick except for those samples with no added quartz would be above the upper limit (110 μg) of the area of interest. If all values for brick except for those samples with no added quartz are eliminated, the results in the area of interest are a better fit to the model. Figure 12 shows the adjusted nominal quartz content compared to that derived from the FTIR results, based on FTIR calibration of quartz-only samples using the average of the repeated calibration data.

Figure 12. Plot of nominal quartz content adjusted for quartz in the interference (x-axis) against predicted quartz content from calibrated FTIR values (y-axis) for all results between 25 and 110 μg . Shaded area is 95% confidence interval of the regression line. PDCB represents mixed plaster-drywall-cement-brick samples with quartz added.

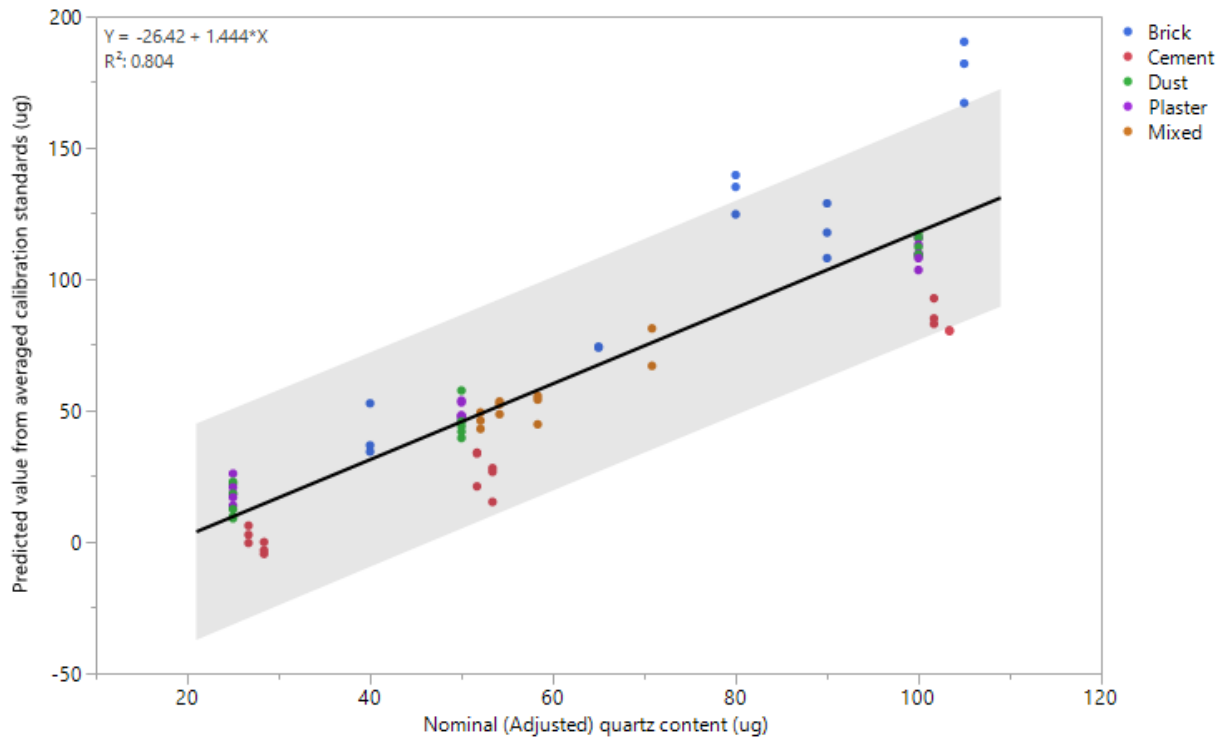
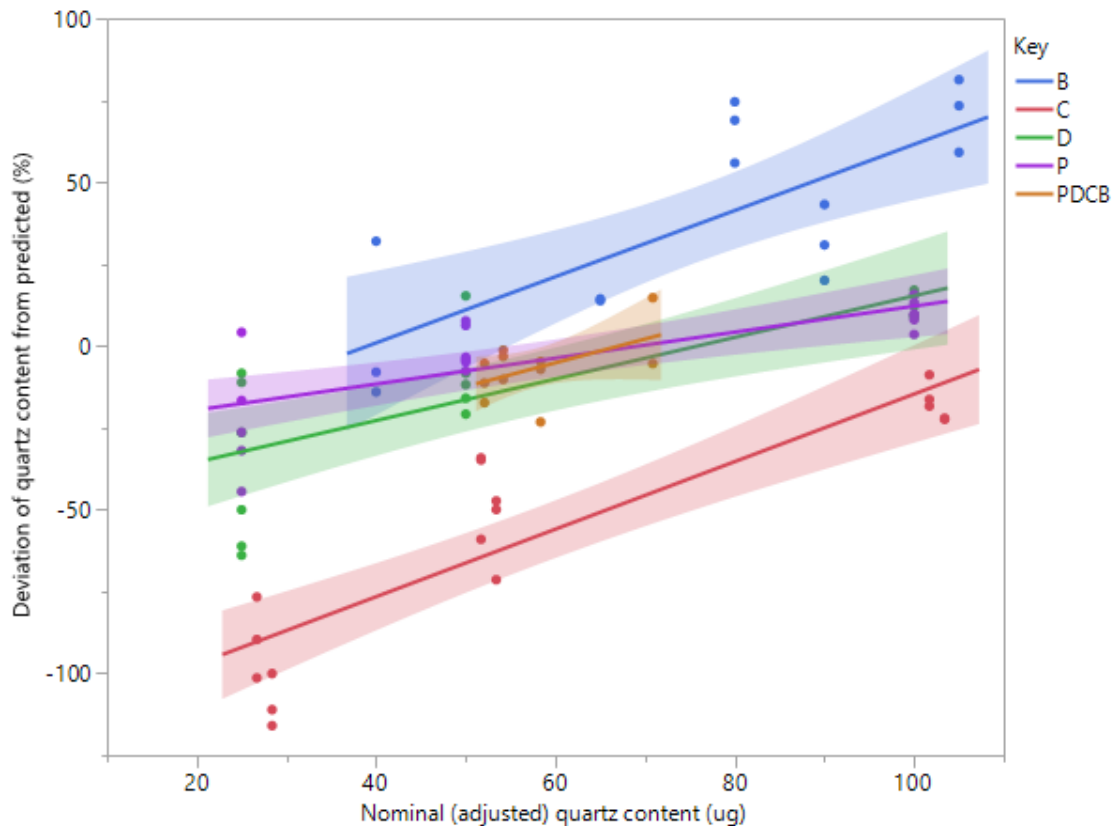


Figure 13 shows the same data plotted as percentage deviation of the calibrated quartz determinations from the adjusted nominal values. This makes clearer the presence of a positive interference for quartz in the brick increases the apparent quartz content of the brick, while the presence of a negative interference in the cement decreases the apparent quartz content of cement, and if the amounts of these interferences were known, through calibration of the interference in a specific region of the FTIR spectrum, the interferences are likely correctable. However, this would require consistency between brick and cement from different sources. This evolution of the procedure is currently employed for mineral interferences in the mine results (Cauda et al., 2018). Two aspects of the data are encouraging. First, of the 70 results in this set, 53 (76%) are within 35% of nominal loadings, 58 (83%) are within 50% of nominal loadings, and 64 (91%) are within 100%. Note that means that a reading of 100 μg is highly likely to be above the PEL, and a reading of 50 μg is highly likely to be above the action level, even when large quantities of interfering dusts are present. Second, the 9 PDCB (plaster-drywall-cement-brick) samples, representing up to 250 μg of each of all four interferences together, with quartz added were all within $\pm 25\%$ of the adjusted nominal values (assuming 8% quartz in brick).

Figure 13 Plot of nominal quartz content adjusted for quartz in the interference (x-axis) against % deviation of calibrated FTIR values from nominal (y-axis) for all results between 25 and 110 μg . Shaded areas represent 95% confidence interval of the regression lines.



CONCLUSIONS

The effects of plaster, drywall, cement and brick matrices on EoS-DoF quartz measurement by FTIR were investigated through two different sample spiking procedures. The first sequential addition procedure led to unsatisfactory results due to non-homogeneous dust distribution. It was observed that the follow-up slurry containing the interference dust could a) push the original quartz away from the center, and b) lead to a generally uneven deposit, leading to highly variable results.

However, the goal of homogeneous distribution was greatly improved by pre-mixing the sample as a single slurry (mixed addition procedure). The results of analyzing the mixed addition samples by FTIR show that a) plaster and drywall dusts do not interfere substantially with the quartz measurement; b) cement does not interfere with the quartz measurement, but a change in the intercept of the correlation suggests an effect on the background absorbance of the filter; and c) in addition to having a substantial quartz content which has to be carefully evaluated in any study, brick dust may also contain an additional material, probably a silicate mineral, which interferes additionally with the quartz peaks. Thus, the presence of cement leads to lower quartz values and brick leads to higher values, but overall, 83% of the quartz contents predicted from the averaged calibration data agreed within 50% of the adjusted nominal loadings. This result is encouraging given the high levels of interfering dusts. Samples loaded with smaller amounts of all four dusts in combination gave even better results, with all nine results within 25% of the adjusted nominal loadings. Both cement and brick could be correctable interferences once the identity of the interference is revealed, in the same way that correction is made for interfering mineral dusts in mines, and this one of the further investigations suggested by this study. It also is important to further investigate the extent of the difference in XRD results from using NIST 1878a or NIST 1878b as the XRD calibration standards. Mixed addition protocol samples have been retained for possible future evaluation by XRD.

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Dr. Emanuele Cauda (NIOSH PMRD) reviewed the study protocol, provided training on the analytical procedure, and reviewed the final manuscript.

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