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High-volume samplers for the assessment of respirable silica content in metal mine dust via direct-on-filter analysis

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ABSTRACT: Exposure to respirable crystalline silica in the mining industry around the world is a recognized occupational hazard. Operators are limited in monitoring exposure to silica by lengthy off-site laboratory analysis of samples. The collection of samples for short periods of time during the worker's shift and subsequent on-site silica quantification would allow for the timely identification of high-risk tasks. With the objective of testing more timely solutions for self-compliance and engineering monitoring, the performance of five different samplers was investigated in a calm-air chamber. The quantification of silica was conducted via direct-on-filter (DoF) analytical techniques, which have the potential to be employed at mine sites, and indirect techniques, currently completed exclusively off-site. The experiments provided data for a statistical evaluation of the efficacy of collecting respirable mine dust and crystalline silica by different samplers and the potential use of a DoF technique for the quantification of respirable crystalline silica on samples collected with high-volume samplers was assessed.

1 INTRODUCTION

Exposure to airborne aerosols in any occupational environment can lead over time to debilitating respiratory diseases that can affect the health of workers. Workers employed in the mining industry can be exposed to high levels of respirable crystalline silica (hereafter called silica) whose exposure is associated with the development of silicosis (Leung et al. 2012), lung cancer (IARC 1997, Straif et al. 2009), other pulmonary tuberculosis, and airway diseases (NIOSH 2002).

Miners' exposure to silica is currently quantified in the United States by collecting a filter sample and submitting it to an analytical laboratory, where it is analyzed by an established method. If the sample was collected in a coal mine, the analysis entails an ashing and Fourier transform infrared (FTIR) process known as the P7 analytical method (Mine Safety Health Administration (MSHA) 2008), while samples from non-coal mines, such as metal mines, are analyzed using an X-ray diffraction (XRD) technique (Mine Safety and Health Administration (MSHA) 2004). Since these methods entail a time lag of weeks before exposure data are received, the information is often of little use to inform modifications to workplace conditions aimed at preventing overexposures.

A more timely silica monitoring approach in mining environments would help to identify high concentration levels and support the assessment of dust control technologies. The National Institute for Occupational Safety and Health (NIOSH) Office for Mine Safety and Health Research (OMSHR) is investigating technologies for field-portable silica monitoring solutions. An analytical technique using a portable FTIR has been investigated recently and showed promising results (Miller et al. 2012, Miller et al. 2013) on the analysis of silica in coal dust samples. Because of the potential application in the field, the technique requires the analysis of the respirable dust, coal or non-coal, collected on a sampling filter without any preparation. This approach, generally called direct-on-filter (DoF) is not new and has been investigated and adopted by several researchers and agencies around the world (HSE - Health and Safety Executive 2005, Kauffer et al. 2005, Pretorius 2011). For any DoF technique, the deposition uniformity of the analyte across the sampled filter is essential (Chen et al. 2010, Miller et al. 2013). The uniqueness of the OMSHR approach is the intention of proposing the technique for on-site monitoring activities.

While a DoF approach can be the foundation for silica field-based monitoring, the collection of a sufficient amount of respirable dust containing silica for the analysis is another pressing issue. This is particularly true for monitoring activities conducted by the operator as self-compliance and engineering checks, where generally the samples are collected for less than a full shift. In such circumstances, high-volume samplers might be a way to collect a sufficient amount of respirable particles for subsequent silica analysis. Samplers currently used in the mining industry are characterized by a flow rate of no more than 2 liters per minute. Samplers with higher flow rates could provide a sufficient amount of analyte in a shorter time. A few evaluations of high-flow samplers for the collection of respirable dust have been published recently (Lee et al. 2010, Eypert-Blaison et al. 2011, Lee et al. 2012, Stacey et al. 2014). The studies showed that different samplers can provide representative respirable samples comparable to the ones collected by the low-volume samplers.

The present study investigates the combined use of high-volume samplers for the collection of mine dust and a DoF technique for the quantification of silica in mine dust. As a first step, the deposition of the dust on the filter media needs to be assessed for each sampler—among the scientific community there is the concern that DoF techniques can be used only with small-size filters. High-volume samplers generally use mid-size filters because of the generated pressure drops. Secondly, the quality of the DoF technique estimation needs to be verified using the P7 analytical method. Finally, the performance of the high-volume samplers in providing representative respirable dust and silica samples needs be verified with mine dust.

2 METHODOLOGY

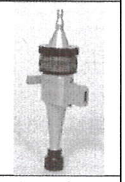
2.1 *Chamber*

The study was conducted in a calm-air chamber (Marple &Rubow 1983) specifically designed for dust sampling investigations. The chamber has a hexagonal cross section 2.44 m high with an inside diameter of 1.19 m. The dust is introduced at the top of the chamber and thoroughly mixed in this region by the energy of an air jet entering at the side of the chamber. From this mixing area, the dust flows downward through a 10-cm-thick honeycomb structure where turbulence in the air is reduced, providing a low-velocity downward flow through the test section portion of the chamber. A table supporting the samplers can be rotated, reducing the effects of any variation in the dust concentration within the chamber. Past work (Marple &Rubow 1983) has shown the sampling zone of the chambers, even without rotation, to be very uniform (relative standard deviation between samples <0.05). Dust collected in a silver mine was aerosolized using a fluidized bed dust generator (3400A, TSI, Shoreview, MN) and dispensed into the chamber. A preliminary study showed that the generated dust has a mass median diameter of 5.5 µm and a geometric standard deviation of 2.3. The respirable fraction of the dust showed 5% silica. Before entering the chamber, the aerosol was neutralized by an NRC Aerosol Neutralizer (3012A TSI).

2.2 *Samplers*

Two low-volume samplers and three high-volume samplers were used in the study. The low-volume samplers were the 10-mm nylon Dorr-Oliver (DO) cyclone (Sensidyne, Clearwater, FL, USA) and the Higgins-Dewell (HD) cyclone (model: BGI4, BGI USA Inc., Waltham, MA, USA). The three high-volume samplers were the GK2.69 (BGI Inc., Waltham, Massachusetts, USA), the GK4.162 (BGI Inc., Waltham, Massachusetts, USA), and the FSP10 (Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA), Sankt Augustin, Germany). The samples were collected on 5-µm pore size 37-mm PVC filters (GLA5000, SKC Inc., Eighty Four, PA, USA) except the GK4.162. Samples for the GK4.162 were collected on 5-µm pore size 47-mm PVC filters (GLA5000, SKC Inc.). The flow rate for each sampler was ensured by the use of a centralized vacuum pump and critical orifices (BGI Inc.). The nominal flow rates for each sampler are reported in Table 1.

Table 1. The five dust samplers used for this study.

10-mm nylon cyclone -DO	BGI4L cyclone - HD	GK2.69	GK4.162	FSP10
				
1.7 lpm	2.2 lpm	4.4 lpm	9 lpm	11.2 lpm
37mm filter	37-mm filter	37-mm filter	47-mm filter	37-mm filter

The flow rates for the GK2.69 and FSP10 were optimized following the procedures from previous studies (Lee et al. 2012). Five samplers of each type were simultaneously tested inside the chamber for a total of 25 samplers overall. The samplers were positioned in an annular disposition inside the chamber.

2.3 *Study conditions*

The collection of respirable dust and silica was investigated for each sampler by varying the testing operating variables. Three variables were selected: 1) respirable mass loading; 2) respirable mass concentration during the sampling event; and 3) relative humidity inside the chamber during the sampling event. Three levels of mass loading, with the HD cyclone selected as a reference, were employed; two levels of mass concentration and relative humidity, respectively, were employed. Table 2 summarizes the operating variables for each test. A single test for each set of conditions was conducted.

Table 2. Testing operating conditions.

Test number	Respirable mass loading (HD reference)	Respirable mass concentration	Relative humidity (Rh)
1	0.4 mg	2 mg/m^3	50%
2	1 mg	2 mg/m^3	50%
3	2 mg	2 mg/m^3	50%
4	0.4 mg	4 mg/m^3	50%
5	1 mg	4 mg/m^3	50%
6	2 mg	4 mg/m^3	50%
7	0.4 mg	2 mg/m^3	80%
8	1 mg	2 mg/m^3	80%
9	2 mg	2 mg/m^3	80%

2.4 *Sample analyses*

Samples were equilibrated, neutralized, and pre- and post-weighed in a controlled environment set at 22 ± 0.7 °C and 50% ± 2% relative humidity. Gravimetric analysis of the samples was conducted by a micro balance (XP6, Mettler-Toledo, Columbus, OH, USA) with a precision better than 5 μg, and overall the gravimetric analysis had an LOQ = 14 μg in a single weighing (Page &Volkwein 2009). Blank filters were used to correct the final mass determination.

After the gravimetric analysis, the samples were analyzed via a DoF technique developed by OMSHR (hereafter DoF-OMSHR) (Miller et al. 2012, Miller et al. 2013). The technique is focused on the use of a portable FTIR spectrometer (Alpha, Bruker) in transmission mode. The method entails mounting the filter in a stainless steel holder placed so that the filter is centered between the horizontal IR source beam and the detector, where the beam has a 6-mm focal diameter. The FTIR resolution has been optimized at 4 cm-1. The DoF-OMSHR technique was recently used for the successful quantification of silica in coal mine dust samples collected with 10-mm nylon DO cyclones and 37-mm filters. An excellent linearity was found between the area of the characteristic silica IR doublet assessed via the single analysis of the center of the filter and the entire quantity of silica deposited on the filter.

A second study showed the importance of the deposition of silica across the filter for its quantification via the DoF-OMSHR technique (Miller et al. 2013). The accurate quantification of silica deposited on the filter is possible via the analysis of the center of the filter only if the deposition profile is known and consistent. For this reason, the deposition of silica across the filters in the five samplers used in this study was investigated. The investigation was conducted by using a 9-point protocol previously tested (Miller et al. 2013). The stainless steel holder containing the filter was vertically adjusted in 3-mm increments to allow analyses at nine locations across the centerline of the filter. IR analyses were conducted at 3-mm intervals (center-to-center overlap of the 6-mm beam), with the fifth shot at the filter center. The intensity of silica signal, in terms of area of the characteristic silica FTIR doublet, in each of the nine points was used to determine the deposition profile for each sampler under each of the first six tests. The effect of the relative humidity on the deposition across the filter is assumed to be minor.

In a second separate phase, the DoF-OMSHR technique was used to estimate the amount of silica collected by the five samplers in each test. The quantification via the DoF-OMSHR technique was conducted by analyzing only the center of the filter. As described above, the calibration for the technique has been established only for the DO cyclone (Miller et al. 2012) with its specific filter deposition. For this reason, the information on the silica deposition across the filter for the other four samplers was used to adjust the DoF-OMSHR estimation.

Finally, a representative portion of filters collected by the five samplers during the first six tests were sent to an external lab where XRD analysis was carried out according to the NIOSH 7500 method for quantification of silica (NIOSH 2003).

3 RESULTS AND DISCUSSION

The results of the quartz deposition analysis across the filter for each sampler are presented in Figure 1. The silica intensity data were normalized with the first point that is the farthest from the center. Point number five was verified to be the center of each filter. The profiles indicate the uniformity and consistency of the deposition of silica on the filter. The deposition is radially symmetric for all five samplers. This is a very important preliminary step for the implementation of a single-point transmission FTIR analysis on the collected dust for the estimation of silica.

The deposition profiles for DO cyclones are inline with the finding of a previously published work (Miller et al. 2013). The deposition is more intense in the center of the filter but the relative abundance is not affected by the respirable dust loading. The deposition profile is also not affected by the respirable mass concentration. The HD cyclones show a similar deposition profile but the relative abundance seems to be affected by both the respirable dust loading and mass concentration.

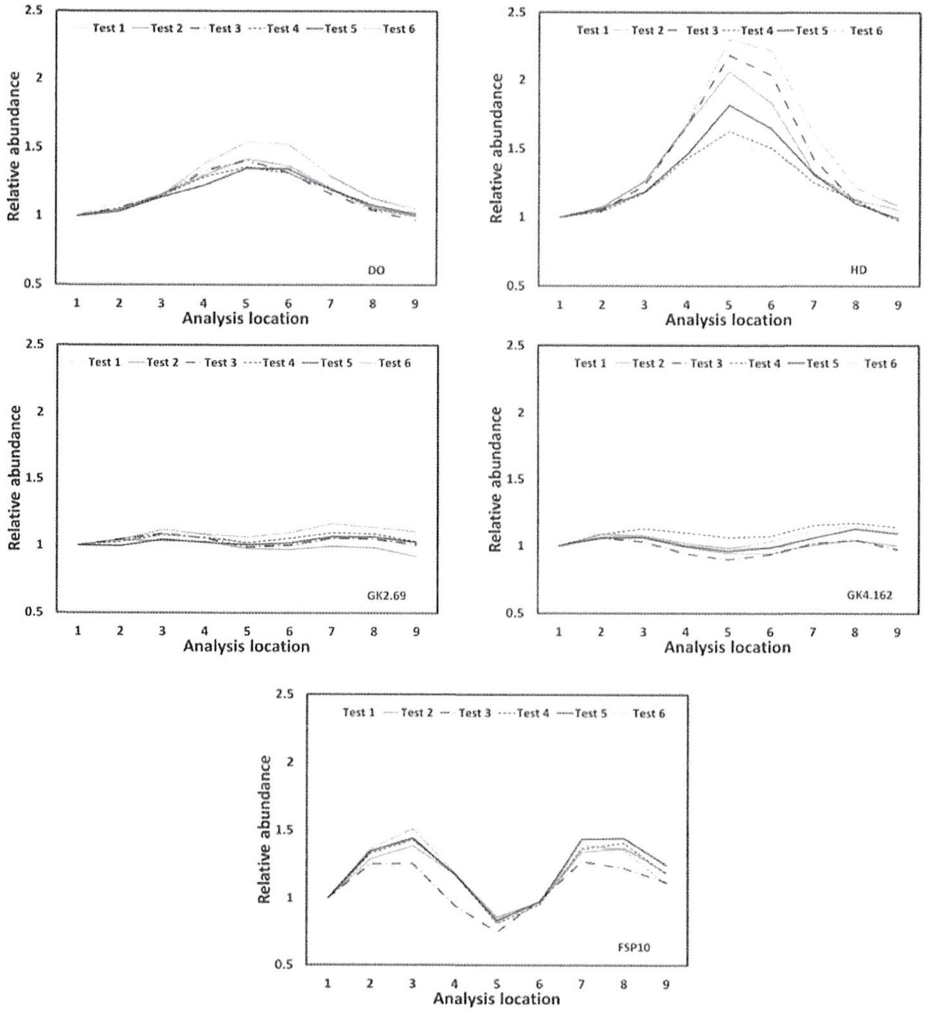


Figure 1. Averaged deposition profiles for silica for the five samplers from top to bottom: 10-mm nylon DO cyclone, BGI4L HD cyclone, GK2.69, GK4.126, and FSP10.

A more centric silica deposition profile was found in higher mass concentrations or mass loadings on the filter.

This characteristic of the HD cyclone can potentially be an issue for the DoF-OMSHR technique via FTIR single-point analysis of the center of the filter—i.e., the single-point analysis assumes a constant and known deposition. In the case of the HD cyclone, the deposition profile should be derived by the respirable mass concentration and mass loading information, and this information is generally not available in the field. The samples collected with the GK2.69 and GK4.162 present uniform and consistent silica deposition profiles. The difference in relative abundance for different points on the filter is less than 10%. In addition, the profiles were not a function of either mass loading or mass concentration levels. This characteristic is optimal for potential use in combination with the DoF-OMSHR technique. Finally, the deposition profile of the samples collected with the FSP10 is still radially symmetric but the center is lighter in loading. This specific and unique profile was not found to be affected by the mass loading or mass concentration. It is possible that the vortex of the cyclone creates this effect in the center of the filter.

The results of the gravimetric analysis were used to calculate the respirable mass concentration detected by each sampler in different experimental conditions. The data from the three high-volume samplers were then compared to the data obtained by the two low-volume samplers. A univariate analysis considering the mass concentration data as dependent variable and the test conditions and the samplers as fixed variable was used (alpha =0.01; SPSS). Figure 2 summarizes the average ratios and confidence levels (alpha 0.01) for th comparison.

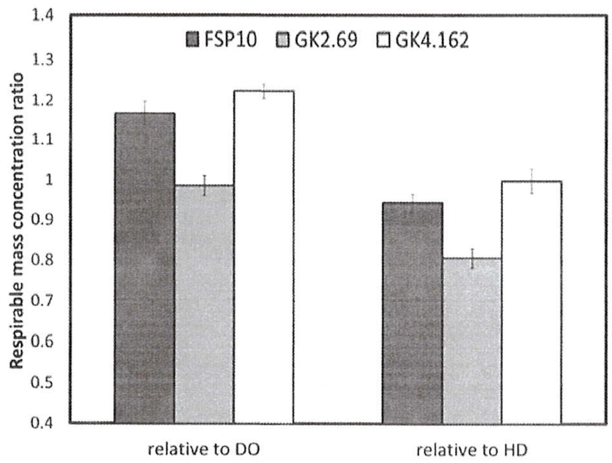


Figure 2. Average and confidence level of respirable dust mass concentration ratios of the high-volume samplers (FSP10, GK2.69, and GK4.162) to low flow rate samplers (DO and HD cyclones).

The FSP10 and the GK4.162 samplers on average oversampled dust compared to the respirable DO cyclone, while the respirable mass concentration assessed by the GK2.69 was not significantly different from the DO cyclone. The finding is different when mass concentration data are compared to the HD cyclone: In this case the FSP10 and the GK2.69 undersampled while the GK4.162 was not significantly different from the HD cyclone. The different effects can be explained by the different penetration efficiencies of the five samplers. The ratio is the result of the sampler penetration applied to the particle size distribution of the dust.

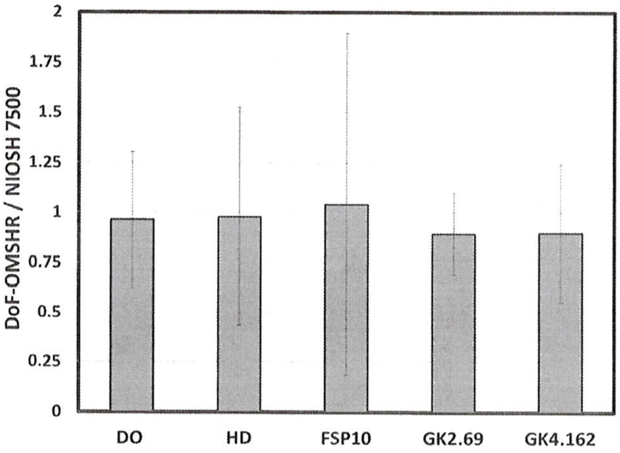


Figure 3. Average and confidence level of silica mass concentration ratios of the DoF estimation and NIOSH7500 values for the five samplers tested.

The second part of the analysis on the collected samples was the estimation and quantification of silica. More than half of the samples collected in the first four tests (Table 1) were analyzed via the DoF-OMSHR technique, followed by the NIOSH7500 method. The results of the two analyses were used to assess the quality of the DoF-OMSHR estimation for each sampler (Figure 3). On average, the estimation assessed more than 90% of the quantity measured via the standard analysis.The GK2.69 showed the lowest confidence interval among the samplers and this can be related to the extremely uniform distribution across the filter displayed by the two samplers.

The performance of the high-volume samplers in collecting silica samples by comparison to that of the low-volume samplers was assessed by using the average silica mass concentration data obtained during different testing conditions (Figure 4). For this comparison, only the DoF-OMSHR technique results were used. The respirable silica concentration measured by the high-volume samplers is on average close to that measured by the DO cyclone. The univariate analysis (alpha 0.01) showed that the ratios were not significantly different for all three high-volume samplers. While the ratio for the GK2.69 sampler is in line with the one presented in Figure 2 for respirable mass concentration ratio, the ratios for the FSP10 and GK4.162 are substantially lower compared to the levels in Figure 2.

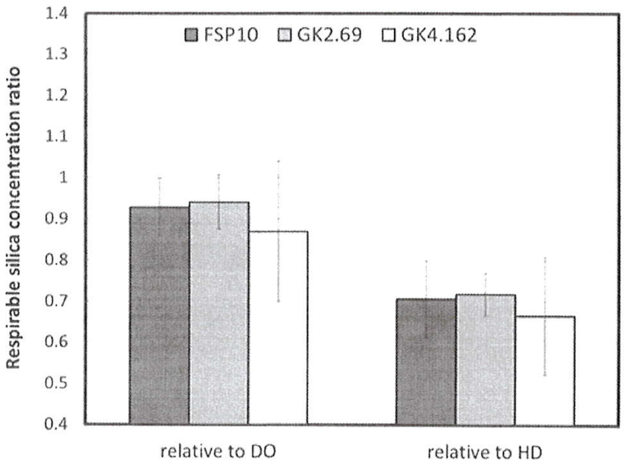


Figure 4. Average and confidence level of silica mass concentration ratios of the high-volume samplers (FSP10, GK2.69, and GK4.162) compared to low-flow rate samplers (DO and HD cyclones).

An explanation for the above results can be proposed but it requires two assumptions: 1) the content (percent) of silica is not constant in the dust and it varies with the size of the particles and 2) the percentage of silica in larger-size particles is substantially lower than the average. As described above, the overestimation of respirable dust concentration shown by the FSP10 and GK4.162 compared to the DO cyclone is induced by higher penetration efficiencies of these samplers for large particles close to the respirable convention. Figure 4 shows that, in the case of silica, the effect of higher penetration is minimized. To support this explanation, a comprehensive and size-segregated analysis of the dust would be necessary. Unfortunately a similar analysis is extremely complex and not exempt from biases. Nevertheless, the results show that the three high-volume samplers can provide respirable silica samples comparable to the DO cyclone for this specific dust, but only the GK2.69 is capable of providing comparable respirable dust samples.

The ratios in Figure 4 relative to the HD cyclone show different effects: All three high-volume samplers collected significantly less silica than the HD cyclone, and this is also true for the GK4.162, which was found to measure the same respirable mass concentration (Figure 2). Penetration curves and assumed size-dependent silica content in the dust cannot explain this effect. To investigate the causes, the respirable dust mass and silica net mass ratios for the high-volume samplers compared to the low-volume sampler were assessed (Figure 5). The data presented are the average ratios of the net masses collected by the high-volume samplers compared to the low-volume samplers for both respirable dust and silica, respectively. In other words, the ratios represent the average relative increase in sample collection by the high-volume sampler.

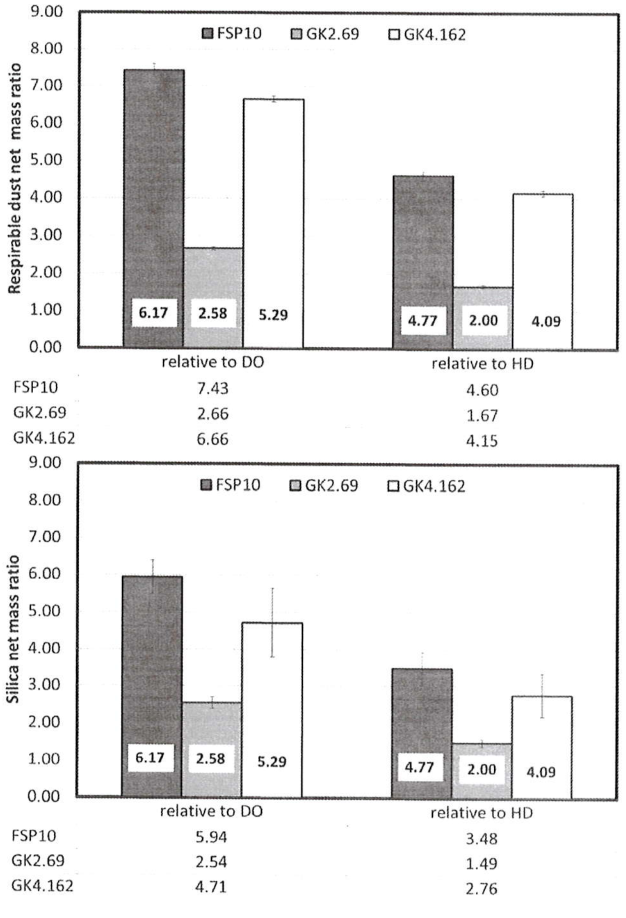


Figure 5. Average and confidence level of respirable dust and silica net mass ratios of the high-volume samplers (FSP10, GK2.69, and GK4.162) compared to low-volume samplers (DO and HD cyclones).

In each chart in Figure 5, the white boxes indicate the ratios based on the average measured flow rates of the samplers. Those values represent the theoretical increase in sample collection by the high-volume samplers caused only by a higher flow rate. The panel on the left refers to the respirable dust net mass ratio while the panel on the right refers to the silica net mass ratio. The actual net mass ratios tend to confirm the interpretation given in the previous paragraphs. The GK2.69 sampler collects around 2.6 times more than the DO cyclone in terms of both respirable dust and respirable silica, and this value corresponds to the flow rate increase. The FSP10 and GK4.162 collected amounts of silica in line with the increase of flow rates, but they oversampled the respirable fraction for this specific dust.

The average amount of silica collected by the high-volume samplers compared to the low-volume HD cyclone was substantially lower than the theoretical increase induced by the higher flow rate. Wall losses in the sampling cassettes for the high-volume samplers could explain this effect if diffusion of small particles, more rich in silica, is the phenomenon. But if the high-volume samplers are subject to wall losses and they collected the same amount of silica relative to the DO cyclone, then the DO cyclone should be affected too. The direct comparison of dust net mass ratio and silica net mass ratio for DO and HD cyclones confirm this explanation (Figure 6). The theoretical net mass increase based on the increased flow rate from the DO to the HD cyclones should be 1.29; however, the gravimetric analysis of the samples shows an actual average increase of 1.61. This discrepancy is simply the effect of different penetration efficiencies applied to the specific dust. The analysis on silica shows that the HD cyclone collected 1.75 times more silica than the DO cyclone. This could be explained by electrostatic wall losses for the DO cyclone.

4 CONCLUSIONS

Five samplers, two low-volume and three high-volume, were tested for the collection of respirable mine dust and silica in calm-air chamber testing. Testing variables were the respirable mass concentration, the respirable mass loading, and the relative humidity. A recently developed DoF technique was used to estimate the amount of silica in the collected samples. The study of the deposition of silica on the filters showed that all the samplers provide a uniform deposition of silica across the filter. Only the HD cyclone showed a deposition that was affected by the testing variables. The deposition for the high-volume samplers GK2.69 and GK4.162 was found to be the most consistent across the filter and this characteristic can benefit a DoF technique. The comparison of the FTIR method and the results of the NIOSH7500 analysis shows that the DoF approach can be used successfully with the DO, GK2.69, and GK4.162. The results were more complicated for the HD and FSP10 cyclones because of inconsistent and non-uniform distribution of the filter deposit (Figure 2). The three high-volume samplers collected comparable amounts of silica compared to the DO cyclone, but only the GK2.69 collected a comparable amount of respirable dust. The different penetration efficiency of the samplers and higher presence of silica in the smaller-size fraction of the dust can explain this result. All the high-volume samplers collected substantially less silica than the HD cyclone and only the GK4.162 collected a comparable amount of respirable dust. This result is more difficult to explain and would require additional testing. A tentative explanation was proposed that involves diffusion wall losses for the samplers. The direct comparison of the results from the two low-volume samplers supports this explanation.

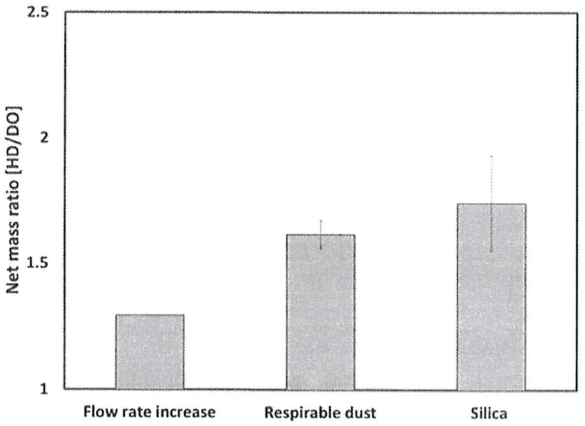


Figure 6. Average and confidence level of respirable dust and silica mass net ratios of HD cyclone to DO cyclone.

5 DISCLAIMER

The mention of any company or product does not constitute an endorsement by the National Institute for Occupational Safety and Health. The findings and conclusions in this paper are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health.

REFERENCES

Chen, C.H., P.J. Tsaia, C.Y. Lai, Y.L. Peng, J.C. Soo, C.Y. Chen and T.S. Shih. (2010) Effects of uniformities of deposition of respirable particles on filters on determining their quartz contents by using the direct on-filter X-ray diffraction (DOF XRD) method. *Journal of Hazardous Materials* 176(1–3):389–394.

Eypert-Blaison, C., J.C. Moulut, T. Lecaque, F. Marc and E. Kauffer. (2011). Validation of the Analysis of Respirable Crystalline Silica (Quartz) in Foams Used with CIP 10-R Samplers. *Annals of Occupational Hygiene* 55(4):357–368.

HSE – Health and Safety Executive. (2005) MDHS 101 – Crystalline silica in respirable airborne dusts Direct-on-filter analyses by infrared spectroscopy and X-ray diffraction.

IARC. (1997) IARC monographs on the evaluation of carcinogenic risks to humans: silica, some silicates, coal dust and para-armid fibrils. Vol 68. Lyon, France: World Health Organization, International Agency for Research on Cancer.

Kauffer, E., A. Masson, J.C. Moulut, T. Lecaque and J.C. Protois. (2005) Comparison of direct (X-ray diffraction and infrared spectrophotometry) and indirect (infrared spectrophotometry) methods for the analysis of alpha-quartz in airborne dusts. *Annals of Occupational Hygiene* 49(8):661–671.

Lee, T., S.W. Kim, W.P. Chisholm, J. Slaven and M. Harper. (2010) Performance of High Flow Rate Samplers for Respirable Particle Collection. *Annals of Occupational Hygiene* 54(6):697–709.

Lee, T., E.G. Lee, S.W. Kim, W.P. Chisholm, M. Kashon and M. Harper. (2012) Quartz Measurement in Coal Dust with High-Flow Rate Samplers: Laboratory Study. *Annals of Occupational Hygiene* 56(4):413–425.

Leung, C.C., I.T.S. Yu and W.H. Chen. (2012) Silicosis. *Lancet* 379(9830):2008–2018.

Marple, V.A. and K.L. Rubow. (1983) An aerosol chamber for instrument evaluation and calibration. *American Industrial Hygiene Association Journal* 44:361–367.

Miller, A.L., P.L. Drake, N.C. Murphy, E.G. Cauda, R.F. LeBouf and G. Markevicius. (2013) Deposition uniformity of coal dust on filters and its effect on the accuracy of FTIR analyses for silica. *Aerosol Science and Technology* 47(7):724–733.

Miller, A.L., P.L. Drake, N.C. Murphy, J.D. Noll and J.C. Volkwein. (2012) Evaluating portable infrared spectrometers for measuring the silica content of coal dust. *Journal of Environmental Monitoring*.

Mine Safety and Health Administration (MSHA) (2004) Xray Diffraction Determination of Quartz and Cristobalite in Respirable Mine Dust Method P2, July 2004.

Mine Safety Health Administration (MSHA). (2008) Infrared Determination of Quartz in Respirable Coal Mine Dust – Method No. MSHA P7. US Dept of Labor-MSHA-Pittsburgh Safety and Health Technology Center.

NIOSH. (2002) NIOSH hazard review: health effects of occupational exposure to respirable crystalline silica. Publication No. 2002–129. Cincinnati, OH: National Institute for Occupational Safety and Health.

NIOSH. (2003) NIOSH manual of analytical methods. 4th edn. Silica, crystalline, by XRD (filter redeposition). Cincinnati, OH: National Institute for Occupational Safety and Health.

Page, S.J. and J.C. Volkwein. (2009) A revised conversion factor relating respirable dust concentrations measured by 10 mm Dorr-Oliver nylon cyclones operated at 1.7 and 2.0 L min-1. *Journal of Environmental Monitoring* 11(3):684–689.

Pretorius, C. (2011) The Effect of Size-selective Samplers (Cyclones) on XRD Response. *Journal of the Mine Ventilation Society of South Africa.*

Stacey, P., T. Lee, A. Thorpe, P. Roberts, G. Frost and M. Harper (2014) Collection Efficiencies of High Flow Rate Personal Respirable Samplers When Measuring Arizona Road Dust and Analysis of Quartz by X-ray Diffraction. *Annals of Occupational Hygiene.* 58(4):512–523

Straif, K., L. Benbrahim-Tallaa, R. Baan, Y. Grosse, B. Secretan, F. El Ghissassi, V. Bouvard, N. Guha, C. Freeman, L. Galichet, V. Cogliano and W.I.A.R.C.M. Workin. (2009) A review of human carcinogens-Part C: metals, arsenic, dusts, and fibres. *Lancet Oncology* 10(5):453–454.