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Quartz Measurement in Coal Dust with High-Flow Rate Samplers: Laboratory Study

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Abstract

A laboratory study was performed to measure quartz in coal dust using high-flow rate samplers (CIP10-R, GK2.69 cyclone, and FSP10 cyclone) and low-flow rate samplers [10-mm nylon and Higgins–Dewell type (BGI4L) cyclones] and to determine whether an increased mass collection from high-flow rate samplers would affect the subsequent quartz measurement by Fourier transform infrared (FTIR) and X-ray diffraction (XRD) analytical procedures. Two different sizes of coal dusts, mass median aerodynamic diameter 4.48 μm (Coal Dust A) and 2.33 μm (Coal Dust B), were aerosolized in a calm air chamber. The mass of coal dust collected by the samplers was measured gravimetrically, while the mass of quartz collected by the samplers was determined by FTIR (NIOSH Manual of Analytical Method 7603) and XRD (NIOSH Manual of Analytical Method 7500) after one of two different indirect preparations. Comparisons between high-flow rate samplers and low-flow rate samplers were made by calculating mass concentration ratios of coal dusts, net mass ratios of coal dusts, and quartz net mass. Mass concentrations of coal dust from the FSP10 cyclone were significantly higher than those from other samplers and mass concentrations of coal dust from 10-mm nylon cyclone were significantly lower than those from other samplers, while the CIP10-R, GK2.69, and BGI4L samplers did not show significant difference in the comparison of mass concentration of coal dusts. The BGI4L cyclone showed larger mass concentration of ~9% compared to the 10-mm nylon cyclone. All cyclones provided dust mass concentrations that can be used in complying with the International Standard Organization standard for the determination of respirable dust concentration. The amount of coal dust collected from the high-flow rate samplers was found to be higher with a factor of 2–8 compared to the low-flow rate samplers but not in direct proportion of increased flow rates. The high-flow rate samplers collected more quartz compared to low-flow rate samplers in the range of 2–10. There was no significant difference between the per cent (%) quartz in coal dust between the

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FTIR and XRD analyses. The findings of this study indicated that the increased mass of quartz collected with high-flow rate samplers would provide precise analytical results (i.e. significantly above the limit of detection and/or limit of quantification) compared to the mass collected with low-flow rate samplers, especially in environments with low concentrations of quartz or where short sampling times are desired.

Keywords

coal dust; CIP10-R; FSP10; FTIR; GK2.69; high-flow rate sampler; quartz; silica; XRD

INTRODUCTION

Analysis of respirable coal mine dust air samples for crystalline silica with infrared (IR) spectroscopy was initiated by the Federal Coal Mine Health and Safety Act of 1969 (1969 Act) and the Mine Safety and Health Administration measures quartz in >10 000 samples every year. The standard method for measurement in coal mine dust has been revised to improve the precision of the analysis over 30 years (Ainsworth, 2005). The occupational exposure limit of respirable crystalline silica continues to be lowered as a result of improvements in understanding health effects. The National Institute for Occupational Safety and Health (NIOSH) has a recommended exposure limit (REL) value of 0.05 mg m⁻³ since 1974 (NIOSH, 2002). A threshold limit value (TLV) for silica of 0.025 mg m⁻³ was accepted by the American Conference of Governmental Industrial Hygienists (ACGIH) in 2006 (ACGIH, 2006). The Occupational Safety and Health Administration (OSHA), which currently enforces a permissible exposure limit (PEL) for respirable dust based on its silica content (equivalent to 0.1 mg m⁻³ for pure quartz or 0.05 mg m⁻³ for pure cristobalite), has preliminarily proposed to lower the PEL for respirable quartz to 0.05 mg m⁻³ with an action level of 0.025 mg m⁻³. Proficiency analytical testing (PAT) was initiated in 1972 to improve the accuracy of test results in industrial hygiene laboratories (Shulman *et al.*, 1992) and crystalline silica is one of the substances used in this program. Although laboratory performance has improved over the last couple of decades due to improvements in analytical methodology and PAT sample preparation (Madsen *et al.*, 1995), variation in the overall analytical performance continues to exceed that of other analytes. For example, PAT rounds 130–133 for crystalline silica showed higher relative standard deviations (RSDs) (16–33% RSD) than for metals (<7% RSD in cadmium, zinc, and lead; Feng and Schlecht, 2000; Grunder and Bell, 2000; Grunder, 2001) and organic solvents (<10% RSD for four analytes; Shulman *et al.*, 1996), and it was attributed to the differences in the standard reference materials and calibration methods between the laboratories (Eller *et al.*, 1999b). In another set of rounds (101–132), the RSDs were between 20 and 45% and varied inversely with sampling loading, i.e. smaller sampling loading, larger RSD (Eller *et al.*, 1999a). The lowest loading was 38 µg of silica that is approximately two times the current ACGIH TLV or OSHA proposed action level if the silica is collected with a 10-mm nylon cyclone at 1.7 l min⁻¹ for 8 h. The limit of detection (LOD) is between 5 and 10 µg for Fourier transform infrared (FTIR) and X-ray diffraction (XRD) for quartz analysis but accuracy is known to be poor, particularly at low-filter loadings (30 µg) (Lorberau and Abell, 1995).

In many occupational environments, engineering controls such as wet methods and local exhaust ventilation do provide substantial exposure reductions of respirable crystalline silica (Flynn and Susi, 2003; Akbar-Khanzadeh *et al.*, 2007). Consequently, the silica mass on a typical air sample is reduced and often close to the detection limit. This leads to imprecise measurement as sufficient mass is not obtained on the filter for reliable quantification at lower concentrations or shorter time periods of sampling (Stacey, 2007) with the samplers commonly employed operating at 1.7–2 l min⁻¹. In some cases, if dust loadings on a single filter were considered insufficient for silica analysis, several or more filters from the same task sampled on consecutive days might be combined to provide measurable amounts (Goldberg *et al.*, 1973; Verma *et al.*, 1992). However, this is not a common practice. A previous study tried to increase sensitivity of the IR analysis or to lower the LOD by reducing the pellet size of potassium bromide from 13 to 5 mm using a set of paper rings (Virji *et al.*, 2002). IR analysis has similar sensitivity to XRD analysis for well-characterized samples such as coal dust and XRD is the more commonly used technique where unknown silicate interferences are likely to be present. Adopting high-flow rate samplers might be another way to collect sufficient amount of respirable particles for subsequent silica analysis and these samplers may improve their reliability. In our previous study (Lee *et al.*, 2010), the performance of the high-flow rate samplers including the CIP10-R, GK2.69, and FSP10 was evaluated and the high-flow rate samplers were shown to collect more respirable dust than low-flow rate samplers including the 10-mm nylon and Higgins–Dewell type cyclones. However, collected respirable dusts were not necessarily shown to increase in direct proportion to the increase in flow rates of the samplers. The flow rates of GK2.69 and FSP10 cyclones were adjusted to minimize the bias against the international respirable convention (ISO, 1995), 4.4 and 11.2 l min⁻¹, respectively. Note that this convention is not currently used by OSHA, but it is used in the NIOSH respirable sampling method for Particulates Not Otherwise Regulated, and is endorsed for respirable fraction sampling by the ACGIH. Several countries are conducting tests to investigate high-flow rate samplers for respirable crystalline silica measurement including UK (Stacey and Thorpe, 2009) and France (Eypert-Blaison *et al.*, 2011). However, few have reported findings regarding quartz measurement collected with high-flow rate samplers compared to low-flow rate samplers.

The objective of present study is (i) to measure quartz mass in coal dust using high- (CIP10-R, GK2.69 cyclone, and FSP10 cyclone) and low- (10-mm nylon and Higgins–Dewell type cyclone) flow rate samplers and (ii) to determine whether an increased mass from high-flow rate sampler affects subsequent quartz measurement with FTIR and XRD.

MATERIALS

Low-flow rate samplers

The low-flow rate samplers that were employed in this study were (i) 10-mm nylon cyclone (Sensidyne, USA), particle collection by 5- μ m pore size 37-mm polyvinyl chloride (PVC) filter (GLA5000; SKC Inc., Eighty Four, PA, USA), sampling flow rate at 1.7 l min⁻¹ and (ii) Higgins–Dewell type cyclone [model: BGI4L (nickel plated aluminum body and aluminum grit pot), BGI USA Inc., Waltham, MA, USA], particle collection by 5- μ m pore

size 37-mm PVC filter (GLA5000, SKC Inc.) and sampling flow rate at 2.2 l min^{-1} (Table 1).

High-flow rate samplers

Three high-flow rate samplers for respirable fraction particles employed in this study were (i) CIP10-R (Arelco ARC, Paris, France), particle collection by polyurethane foam cup and sampling flow rate at 10 l min^{-1} , (ii) GK2.69 (BGI Inc., Waltham, MA, USA), particle collection by 5- μm pore size 37-mm PVC filter (GLA5000; SKC Inc.) and sampling flow rate at 4.4 l min^{-1} , and (iii) FSP10 [Berufsgenossenschaftliches Institut für Arbeitssicherheit (BIA), Sankt Augustin, Germany], particle collection by 5- μm pore size 37-mm PVC filter (GLA5000; SKC Inc.), sampling flow rate at 11.2 l min^{-1} (Table 1). Calculated sampling hours for each sampler to obtain $10 \mu\text{g}$ of quartz at half of TLV occupational environment are shown in Table 1.

Test particles

Two different sizes of ground Pittsburgh coal (Peters and Volkwein, 2003; Volkwein *et al.*, 2004) from the Pennsylvania State University's coal collection via Mr Jon Volkwein of the Office of Mine Safety and Health Research, NIOSH, Pittsburgh, PA, USA, were generated in this study. A cyclone at the top of the elutriator of the fluidized bed aerosol generator was utilized to generate the smaller size of coal dust. The size distribution of the coal dust was determined by two different Marple personal cascade impactors (Model 298; Graseby Andersen Samplers, Inc., Atlanta, GA, USA) with three repetitions for each size of coal dust. The mass median aerodynamic diameter (MMAD) of Coal Dust A was $4.48 \mu\text{m}$ and geometric standard deviation (GSD) was 1.80. The MMAD of Coal Dust B was $2.33 \mu\text{m}$ and GSD was 1.79.

METHODS

Coal dust sampling

High- and low-flow rate samplers were placed in a calm air chamber. Samplers did not rotate but the chamber has been validated for spatial variability (Lee *et al.*, 2010). Since the spatial variability from this previous study was in the range of 2.0 and 6.1%, the sampling locations of low- and high-flow samplers were not changed in the present study. The coal dusts were generated using a fluidized bed aerosol generator (TSI Inc., Shoreview, MN, USA). Prior to the sample collection, filters and foams of the samplers were equilibrated at least 72 h in the weighing room which incorporates constant relative humidity and temperature. Pre-weighing was performed with a micro balance (UMT2; Mettler-Toledo, Columbus, OH, USA; readability $0.1 \mu\text{g}$) for PVC filters (SKC Inc.) and a dual range analytical balance (AG245, Mettler-Toledo; readability $10 \mu\text{g}$) for rotating cup with polyurethane foam of CIP10-R sampler. Filters and rotating cups with foams were passed through an electrostatic bar (Mettler-Toledo) before weighing to dissipate static charge. Measurements were made after allowing exactly 120 s for balance stabilization. The pre-weighed filters were assembled in cassettes and leak-checked using a field cassette leak tester (Omega Specialty Instruments). Aircheck PCXR-4 pumps (SKC Inc.) were connected to 10-mm nylon and BGI4L cyclones. Legacy pump (SKC Inc.) and SG 10-2 pump (GSA

Messgerätebau GmbH) were connected to the GK2.69 and FSP10 cyclone, respectively. The flow rates through the samplers were calibrated using a BIOS DryCal Meter (BIOS International Corporation, Butler, NJ, USA) using sampler calibration adapter for FSP10 cyclone and calibration jar (SKC Inc.) for the 10-mm nylon cyclone. The BGI4L and GK2.69 inlet was connected directly to the DryCalMeter. The flow rates were calibrated before and after each sampling to ensure that the flow rate did not change significantly ($\pm 5\%$). The flow rate of the CIP10-R was initially calibrated with a CIP10 Calibration bench (Arelco, ARC) and the rotational speed (r.p.m) of the cup was checked before and after sampling. Five different high and low samplers were placed in the calm air chamber and coal mine dusts were collected simultaneously over the same time period. Three different levels of mass concentrations, below the ACGIH TLV for respirable particles (3 mg m^{-3}), around the TLV, and above the TLV, were tested with three repetitions for each level. The mass concentration of coal dust was determined using coal dust mass, pre- and post-flow rate, and sampling time for each sample obtained after sampling. Sampling duration was dependent on mass concentration level and that was between 30 and 240 min. A total of 270 samples were collected. The filters and rotating cups with foams were equilibrated in the weighing room minimum 72 h before post-weighing.

Sample preparation for FTIR analysis

In order to eliminate organic material from coal dust, the sample must be ashed. Two different ashing procedures were employed including low temperature and muffle furnace ashing since these two procedures are standard procedures for elimination of organic material in samples for quartz analysis using FTIR (Table 2). Otherwise, NIOSH Manual of Analytical Methods (NMAM) 7603 (NIOSH, 2003a) for FTIR analysis and 7500 (NIOSH, 2003b) for XRD analysis were utilized for sample preparation and analysis.

Low temperature ashing

Each post-weighted filter was placed in a 50-ml beaker and ashed in a Plasma-Prep II (Model 11005; SPI Inc., West Chester, PA, USA) for a minimum of 2 h. Coal dusts from the CIP10-R sampler were extracted from the polyurethane foam by rinsing with isopropyl alcohol and extracted coal dusts were deposited onto a 37-mm PVC filter and the filter was ashed by the Plasma-Prep II.

Muffle furnace ashing

Each post-weighted filter was placed in a 30-ml porcelain crucible with lid (Avogadro's Lab Supply Inc., Miller Place, NY, USA) and ashed in a muffle furnace (Model F6010; Barnstead/ThermoLyne, Dubuque, IA, USA) for 2 h at 600°C . The foam from the CIP10-R sampler was placed in a porcelain crucible and the contents of the cup were rinsed with isopropyl alcohol into the crucible. The alcohol was ignited in the crucible under the laboratory fume hood to melt the foam and the crucible with contents was then placed in a furnace at 600°C for 2 h (AFNOR, 2002).

Calibration curve construction of quartz and kaolin

A calibration curve for quartz was constructed by following the NMAM 7603 (NIOSH, 2003a) using respirable α -quartz (SRM 1878a; certified by the National Institute of Standards and Technology). Eight different masses of quartz were prepared with the range of 10–300 μg . A calibration curve for kaolin as an interference dust in quartz analysis was also constructed following NMAM 7603.

Redeposition on DM450 filter and FTIR analysis

The ashed sample was redeposited on a DM Metrical membrane filter (DM450, 0.45 μm , 47 mm; PALL Life Sciences, Ann Arbor, MI, USA) using a custom-made 10-mm funnel. A 25-mm glass fiber filter was placed on the fritted base and two 25-mm DM-450 filters were placed on the top of the glass fiber filter; a 47-mm DM-450 filter was cut into two 25-mm DM-450 filters so that the bottom filter could serve as a blank for FTIR analysis. After setting-up the funnel, isopropyl alcohol was added to the funnel prior to adding the ashed sample. After adding ~25 ml isopropyl alcohol, the sample beaker containing the ashed sample was placed into ultrasonic bath for at least 30 s to ensure homogeneous dispersion. The sample was placed in the filtration funnel and vacuum was applied. During filtration, the sample beaker was rinsed at least two or three times with isopropyl alcohol to remove all dust and the rinse added to funnel. After redeposition, the two DM-450 filters were placed in a petri dish to air dry the filters. Both blank and sample filters were placed on the IR card (International Crystal Laboratories, Garfield, NJ, USA) that has 9.5 mm aperture for FTIR (Thermo Fisher Scientific, Nicolet 6700, Waltham, MA, USA) measurement. Mass of the quartz was quantified by the spectrum at 800 cm^{-1} with baseline between 820 and 670 cm^{-1} and interference from kaolin was subtracted at the 914 cm^{-1} reading with baseline between 960 and 860 cm^{-1} using the Omnic software package (version 8.1.11; Thermo Fisher Scientific).

XRD analysis

XRD analysis was carried out by the NIOSH contract laboratory according to the NMAM 7500 [silica, crystalline, by XRD (filter redeposition)] (NIOSH, 2003b). Each filter was removed from the filter keeper and transferred to a 15-ml vial. Then, 5 ml of tetrahydrofuran (THF) was added to each vial. The samples were allowed to stand for 5 min before being vortexed for 2 min. After vortexing, the samples were placed in an ultrasonic bath and sonicated for 10 min and then transferred to a silver membrane filter. A silver membrane filter was placed in the vacuum filtration unit. Then, 2 ml of THF was placed on the filter followed by the sample suspension, three vial rinsings, and a final vial cap rinse. Finally, vacuum was applied to deposit the suspension onto the filter. The silver membrane filter was then transferred to an aluminum sample plate and placed in the automated sample changer for analysis by XRD (Rigaku Ultima III X-ray diffractometer with D/MAX 2000 PC software).

Data analysis

Data were analyzed using SAS/STAT software, version 9.2 of the SAS System for Windows (SAS Institute, Cary, NC, USA). A mixed model two-factor (coal dust type by sampler pair)

analysis of variance (ANOVA) was used (Proc Mixed) to conduct the statistical analysis for net mass ratio and quartz mass ratio. The design factors included coal dust type and sampler pair. A mixed model three-factor ANOVA was used to analyze quartz mass from the samplers. The design factors included coal dust type, sampler pair, and ashing method. Experimental run was utilized as a random blocking factor to statistically account for inherent variation from run to run. *Post hoc* comparisons and contrasts which specify significant interaction were carried out using Fisher's least significance tests. Linear regression coefficients for slope of the mass concentration measures between low-flow and high-flow samplers were calculated using Proc Reg. Chi-square analysis was utilized as an omnibus test to determine proportions of samples being above or below the LOD and the limit of quantification (LOQ). Pairwise comparisons of high-flow samplers and low-flow samplers were also analyzed using a chi-square. All differences were considered significant at $P < 0.05$.

RESULTS

Respirable dust mass concentration comparison

Average and standard deviation of respirable dust mass concentration ratios of the CIP10-R, GK2.69, and FSP10 to the 10-mm nylon and BGI4L cyclones when samplers were exposed to Coal Dusts A and B are shown in Fig. 1. The CIP10-R gave higher mass concentrations by ~10 and 3% compared to the 10-mm nylon and BGI4L cyclones, respectively. The GK2.69 cyclone gave higher mass concentrations by 8.5% compared to the 10-mm nylon cyclone, while the mass concentration of the GK2.69 and BGI4L was close to the unity. The FSP10 cyclone gave higher mass concentrations by 22 and 14% compared to the 10-mm nylon and BGI4L cyclones, respectively. The BGI4L cyclone gave higher mass concentrations by ~9% compared to the 10-mm nylon cyclone. By statistical analysis, mass concentrations of the FSP10 cyclone were significantly higher than other samplers ($P < 0.05$) and mass concentrations of the 10-mm nylon cyclone were significantly lower than other samplers ($P < 0.05$). No significant differences were observed between mass concentrations of the CIP10-R, GK2.69, and BGI4L samplers. Results from linear regression analysis with mass concentrations obtained with five different personal respirable samplers are shown in Table 3 and results were similar to the average of mass concentration ratios of high-flow rate samplers to low-flow rate samplers.

Average and standard deviation of respirable dust mass concentration ratios between high- and low-flow rate samplers separated by Coal Dusts A (larger particle size; MMAD $\approx 4.48 \mu\text{m}$) and B (smaller particle size; MMAD $\approx 2.33 \mu\text{m}$) are shown in Fig. 2. When the samplers were exposed to Coal Dust A, the mass concentration ratios of high-flow rate samplers to the 10-mm nylon cyclone showed statistically significant differences from the mass concentration ratios of high-flow rate samplers to the BGI4L cyclone. However, the same statistical result was not produced when the samplers were exposed to Coal Dust B. Average mass concentration ratios of the BGI4L, CIP10-R, GK2.69, and FSP10 samplers to the 10-mm nylon cyclone with Coal Dust A were 1.18, 1.10, 1.11, and 1.25, respectively. Average mass concentration ratios of the 10-mm nylon, CIP10-R, GK2.69, and FSP10 samplers to the BGI4L cyclone with Coal Dust A were 0.87, 0.96, 0.92, and 1.06,

respectively. Average mass concentration ratios of the BGI4L, CIP10-R, GK2.69, and FSP10 samplers to the 10-mm nylon cyclone with Coal Dust B were 1.00, 1.10, 1.07, and 1.20, respectively. Average mass concentration ratios of the 10-mm nylon, CIP10-R, GK2.69, and FSP10 samplers to the BGI4L cyclone with Coal Dust B were 1.02, 1.11, 1.08, and 1.21, respectively.

Net mass comparison

Average and standard deviation of net mass ratios of high-flow rate samplers to low-flow rate samplers when the samplers were exposed to the Coal Dusts A and B are shown in Fig. 3. The CIP10-R, GK2.69, and FSP10 collected 6.42 (5.88 expected based on flow rate ratio), 2.78 (2.58 expected), and 7.99 (6.58 expected) times more coal dust compared to the 10-mm nylon cyclone, respectively, and 4.68 (4.54 expected), 1.99 (2.00 expected), and 5.76 (5.09 expected) times more coal dust than the BGI4L cyclone, respectively. The BGI4L collected 1.4 (1.3 expected) times more coal dust than the 10-mm nylon cyclone. The FSP10 cyclone collected the largest amount of coal dust followed by the CIP10-R, GK2.69, BGI4L, and 10-mm nylon cyclone according to the flow rate order of the samplers. The BGI4L and 10-mm nylon cyclones did not show a significant difference in their net mass collection ($P > 0.05$). Average net mass ratios of the BGI4L, CIP10-R, GK2.69, and FSP10 samplers to the 10-mm nylon cyclone with Coal Dust A were 1.52, 6.42, 2.84, and 8.18, respectively. Average net mass ratios of the 10-mm nylon, CIP10-R, GK2.69, and FSP10 samplers to the BGI4L cyclone with Coal Dust A were 0.67, 4.35, 1.83, and 5.39, respectively. Average net mass ratios of the BGI4L, CIP10-R, GK2.69, and FSP10 samplers to the 10-mm nylon cyclone with Coal Dust B were 1.29, 6.42, 2.74, and 7.82, respectively. Average net mass ratios of the 10-mm nylon, CIP10-R, GK2.69, and FSP10 samplers to the BGI4L cyclone with Coal Dust B were 0.79, 5.02, 2.15, and 6.15, respectively.

Quartz net mass and mass concentration ratio comparison

Average and standard deviation of quartz net mass ratios of high-flow rate samplers to low-flow rate samplers in both FTIR and XRD analyses are shown in Fig. 3. The CIP10-R, GK2.69, and FSP10 collected 6.83 (5.88 expected), 3.39 (2.58 expected), and 9.55 (6.58 expected) times more quartz compared to the 10-mm nylon cyclone, respectively, and 4.74 (4.54 expected), 2.25 (2.00 expected), and 6.41 (5.09 expected) times more quartz than the BGI4L cyclone, respectively. The BGI4L collected 1.56 times more quartz than the 10-mm nylon cyclone. The quartz net mass ratios were close to the coal dust net mass ratios between the samplers. High standard deviation on quartz net mass ratios was attributable to the several outliers.

Average and standard deviation of quartz concentration ratios of high-flow rate samplers to low-flow rate samplers are shown in Fig. 4 and the ratios are similar with mass concentration ratios of coal dust.

Quartz mass from FTIR and XRD analysis

A scatter plot of quartz mass collected with high- and low-flow rate samplers is shown in Fig. 5 along with reference lines of LOD (NMAM 7603; 10 μg) and LOQ (33 μg) of IR. Most quartz masses collected with the 10-mm nylon and BGI4L cyclones were below the IR

LOQ, i.e. 93 and 83%, respectively. On the other hand, only 22, 57, and 13% of the quartz masses were below the IR LOQ for the CIP10-R, GK2.69, and FSP10, respectively. Approximately 48 and 37% of samples were below LOD for 10-mm nylon cyclone and the BGI4L cyclone, respectively. Generally, significantly ($P < 0.0001$) more data points from high-flow rate samplers were distributed above the IR LOQ than those from low-flow rate samplers indicating that utilizing high-flow rate samplers might provide more precise results in quartz measurement. Some samples that are lower than LOD from NMAM 7603 are shown in Fig. 5 since the LOD and LOQ (1–2% RSD with 5–8 μg of quartz) of our laboratory are ~ 1.5 and $5 \mu\text{g}$ of quartz, respectively. A scatter plot of quartz mass collected with high- and low-flow rate samplers with reference lines of LOD (NMAM 7500; $5 \mu\text{g}$) and LOQ ($16.5 \mu\text{g}$) of XRD analysis is shown in Fig. 6. The quartz masses from XRD analysis showed similar results to those from FTIR analysis. Most of quartz masses were above the XRD LOD in both high- and low-flow rate samplers but quartz masses from high-flow rate samplers were above the LOQ. However, it should be noted that half of quartz masses from the 10-mm nylon cyclone samples were below the LOD and 28% of the BGI4L cyclone samples were below the LOD, which are not shown in Fig. 6.

Quartz content comparison

Quartz mass was divided by net mass of coal dust and multiplied by 100 for the calculation of quartz content (%). Average and standard deviation of quartz content for the entire data set was $7.4 \pm 2.2\%$. Quartz content by FTIR and XRD analysis were $7.2 \pm 1.7\%$ ($n = 179$) and $8.6 \pm 5.6\%$ ($n = 73$), respectively, and no significant difference was found in quartz content between FTIR and XRD analysis. Quartz content by different ashing methods, i.e. low temperature and muffle furnace were 7.0 ± 1.3 and $7.5 \pm 2.1\%$, respectively, and no significant difference was found between ashing methods (Fig. 7). Quartz content between Coal Dusts A and B was 7.6 ± 2.2 and $7.6 \pm 4.4\%$, respectively. The large average and standard deviations of quartz content (%) in XRD analysis were attributable to two outliers, 23 and 50% of quartz. If the outliers are removed from the data set, all the quartz contents separated by analysis method were comparable and with smaller standard deviation ($7.8 \pm 2.1\%$).

DISCUSSION

Mass concentration ratio comparison

Our previous study (Lee *et al.*, 2010) reported that the average mass concentration ratio of the FSP10 to the 10-mm nylon cyclone was 1.85 when the samplers were challenged with aluminum oxide [MMAD = $4.45 \mu\text{m}$, measured with an Aerodynamic Particle Sizer (APS)] with flow rate of 10 l min^{-1} but the average mass concentration ratio of the samplers in the present study was 1.25 with Coal Dust A (MMAD = $4.48 \mu\text{m}$, measured by Marple cascade impactor) by adjusting flow rate of the FSP10 cyclone to 11.2 l min^{-1} . Adjusting flow rate in GK2.69 cyclone produced similar results. The average mass concentration ratio of the GK2.69 to the 10-mm nylon cyclone was decreased to 1.11 (with 4.4 l min^{-1} ; with Coal Dust A) from 1.38 (with 4.2 l min^{-1} ; with aluminum oxide) by adjusting the flow rate. Utilizing adjusted flow rates for the GK2.69 and FSP10 cyclones may provide mass concentration ratios between high- and low-flow rates samplers closer to unity compared to

the flow rates provided by the manufacturers. The mass concentration ratios of high-flow rate samplers to the 10-mm nylon and BGI4L cyclone were statistically non-significant when the MMAD was lower, i.e. when the samplers were exposed to the Coal Dust B (Fig. 2). It could be attributed to the sampling efficiency and different cut point ($_{50}d_{ae}$) of the samplers, i.e. the sampling efficiencies of personal respirable samplers were close to each other in the aerodynamic particle size range of 2 and 4 μm . Decreased mass concentration ratios of the FSP10 to 10-mm nylon cyclone might be explained by changing of $_{50}d_{ae}$ to a smaller size from 4.8 μm (10 l min^{-1}) to 4.3 μm (11.2 l min^{-1}). In accordance with linear regression analysis between the samplers (Table 3), the FSP10 gave significantly higher dust mass concentrations, 19 and 14%, compared to the 10-mm nylon and BGI4L cyclones, respectively. The CIP10-R and GK2.69 samplers, however, showed non-significant difference in performance compared to the low-flow rate samplers. The present study confirmed that the adjusted flow rates for the GK2.69 and FSP10 minimize the bias compared to the flow rates recommended by the respective manufacturers. Therefore, adjusted flow rates of 4.4 l min^{-1} for the GK2.69 and 11.2 l min^{-1} for the FSP10 are recommended for personal exposure assessment of quartz. This was further investigated by calculation of the respirable fraction collected by the samplers and comparing it to the proportion of the mass-weighted ISO respirable size fraction of Coal Dust A obtained from the size distribution data from the Marple cascade impactors. The sampling efficiency of FSP10 was from our previous study (Lee *et al.*, 2010) with monodisperse ammonium fluorescein particles and that of the 10-mm nylon cyclone was from measurement with APS and potassium sodium tartrate particles (Chen and Huang, 1999). The respirable fraction calculated by the mean sampling efficiency of the samplers was multiplied by normalized mass-weighted size distribution ($dm/\Sigma M$) of Coal Dust A. The calculated respirable fraction of FSP10, ISO respirable convention, and 10-mm nylon cyclone was 64.9, 58.5, and 59.9%, respectively. The FSP10 would collect 10.9 and 8.3% more coal dust compared to the ISO respirable convention and 10-mm nylon cyclone, respectively, and 10-mm nylon cyclone would collect 2.4% more compared to ISO respirable convention. Both cyclones meet the accuracy required for exposure assessment of respirable dust compared to ISO respirable convention. The mass concentration ratio differences between the calculated respirable fraction from the Marple impactor data and the mass concentration ratios of Coal Dust A found with the different samplers are shown in Fig. 8.

Quartz mass with high- and low-flow rate samplers

If a 10-mm nylon cyclone collected 10 μg (LOD of IR) of quartz in a full work shift (12 $\mu\text{g m}^{-3}$ with 1.7 l min^{-1} and 8-h sampling), the CIP10-R, GK2.69, and FSP10 might collect ~63, 30, and 88 μg of quartz, respectively, based on the results of the present study. The RSD for crystalline silica was 16–33% for the PAT round 130–133 (silica loading of 22–240 μg) and 20–45% for the PAT round 101–132 (silica loading of 38–173 μg), which showed an inverse relationship with sample loading (Eller *et al.*, 1999a). Workplace Analysis Scheme for Proficiency (WASP) study reported average and median within-laboratory RSD for quartz measurement in both direct and indirect analytical methods was 11.5 and 9.4%, respectively, with quartz loading of 60–460 μg and the RSD was inversely proportional to the mass loading of quartz (Stacey *et al.*, 2003). The detection limits of FTIR and XRD are between 5 and 10 μg but accuracy is poor at low filter loadings of quartz (< 30 μg) (Lorberau

and Abell, 1995). The RSDs from WASP are relatively low since the WASP used larger quartz loading for the tests. If the mass of quartz was 60 µg on the filter collected using a 10-mm nylon cyclone for 8 h (the lowest mass loading in the WASP study), the mass concentration of quartz would be 73.5 µg m⁻³, which is larger than current TLV and REL. It is expected that utilizing high-flow rate samplers for quartz measurement might provide more quartz for subsequent analysis and precise results for personal exposure assessment. Since the high-flow rate samplers require heavier pumps and some samplers are themselves bulky (for example, the FSP10 cyclone), the samplers might interfere with a worker's activity. A future study is necessary to check the feasibility of substitution in practice.

Analysis methods comparison

Pickard *et al.* (1985) reported a linear relationship between quartz mass with IR and XRD analyses for three different occupational environments and most of the samples were statistically non-significantly different showing similar precision and sensitivity. Lorberau *et al.* (1990) compared two direct-on-filter methods with XRD analysis, direct-on-silver membrane filter, and direct-on-mixed cellulose ester (MCE) filter to NMAM 7500 with mineral ore dust in the range of 200–1200 µg. Both direct-on-filter methods showed non-significant difference from NMAM 7500 within 25% (MCE filter) and 30% (silver membrane filter) with 95% of confidence interval. Verma *et al.* (1992) compared Ontario Ministry of Labour method (direct filter analysis by XRD) to NMAM 7602 (indirect filter by IR) in an underground gold mining environment and considered that the two methods are similar when the same calibration material is used. Eller *et al.* (1999a) showed statistically non-significant difference between the IR and XRD analytical methods on silica samples in the PAT. Stacey *et al.* (2003) compared differences of quartz masses between direct-on-filter XRD analysis and direct-on-filter IR analysis in the proficiency testing and no statistical difference was found. Kauffer *et al.* (2005) investigated the difference between direct method of XRD and IR and indirect method of IR and found statistically no significant difference between the methods with quartz dust. However, they observed 13% underestimation of the mean content of silica in the industrial dust from the indirect IR method compared to the mean of the direct XRD and IR methods due to the calcinations during the ashing process. It is not easy to compare directly the present to previous studies since the present study did not use the same samples for both analytical methods. The only way to compare between the FTIR and XRD analyses is to use quartz content (%) by normalizing with net mass of the coal dust. The quartz content between the FTIR and XRD analyses were not significantly different ($P > 0.05$), which is consistent to the previous studies.

CONCLUSIONS

High- and low-flow rate samplers were challenged for collection of two different sizes of coal dust and quartz mass was determined by the FTIR and XRD methods. Mass concentrations of coal dust from FSP10 cyclone were significantly higher than those from other samplers and mass concentrations of coal dust from 10-mm nylon cyclone were significantly lower than those from other samplers. However, the CIP10-R, GK2.69, and BGI4L samplers did not show significant difference in the comparison of mass

concentration of coal dusts. All samplers met the requirements for accuracy for sampling the ISO respirable convention. Adopting high-flow rate samplers would collect more respirable particles but not in the direct proportion to the increased flow rates of the samplers. The additional sample collected by higher flow-rate samplers did not result in an excessive matrix of dust that could interfere with quartz analysis in the indirect preparation method. Thus, the increased mass of interest sample would lead to an improvement in the accuracy of quartz measurements using either the FTIR method or the XRD method, especially in environments with low concentrations of quartz or where short sampling times are desired.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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References

- Ainsworth S. Infrared analysis of respirable coal mine dust for quartz: thirty-five years. *J ASTM Int.* 2005; 2:1–14.
- Akbar-Khanzadeh F, Milz S, Ames A, et al. Crystalline silica dust and respirable particulate matter during indoor concrete grinding—wet grinding and ventilated grinding compared with uncontrolled conventional grinding. *J Occup Environ Hyg.* 2007; 4:770–9. [PubMed: 17763068]
- ACGIH. Threshold limit values (TLVs) and biological exposure indices (BEIs). Cincinnati, OH: American Conference of Governmental Industrial Hygienists; 2006.
- AFNOR. Workplace air: determination by infrared spectrometry Fourier transform crystalline silica: sampling device rotating cup or a membrane filter. Saint-Denis, France: Association Française de Normalisation; 2002. AFNOR XP X 43-243
- Chen CC, Huang SH. Shift of aerosol penetration in respirable cyclone samplers. *Am Ind Hyg Assoc J.* 1999; 60:720–9.
- Eller PM, Feng HA, Song RGS, et al. Proficiency Analytical Testing (PAT) silica variability, 1990–1998. *Am Ind Hyg Assoc J.* 1999a; 60:533–9.
- Eller PM, Key-Schwartz RJ, Song R, et al. Silica method modifications for improved interlaboratory precision. *Synergist.* 1999b; 10:23–4.
- Eypert-Blaison C, Moulut JC, Lecaque T, et al. Validation of the analysis of respirable crystalline silica (Quartz) in foams used with CIP 10-R samplers. *Ann Occup Hyg.* 2011; 55:357–68. [PubMed: 21257743]
- Feng HA, Schlecht P. Proficiency analytical testing (PAT) program. *Am Ind Hyg Assoc J.* 2000; 61:114–1.
- Flynn MR, Susi P. Engineering controls for selected silica and dust exposures in the construction industry—a review. *Appl Occup Environ Hyg.* 2003; 18:268–77. [PubMed: 12637237]
- Goldberg SA, Raymond LD, Taylor CD. Bureau of Mines procedure for analysis of respirable dust from coal mines. *Am Ind Hyg Assoc J.* 1973; 34:200–5. [PubMed: 4354025]
- Grunder FI. PAT program report: background and current status. *Am Ind Hyg Assoc J.* 2001; 62:103–4.

- Grunder FI, Bell C. Proficiency analytical testing (PAT) program June 2000. *Am Ind Hyg Assoc J*. 2000; 61:757–8.
- ISO Standard 7708. Air quality—particle size fraction definitions for health-related sampling. Geneva, Switzerland: International Organization for Standardization; 1995.
- Kauffer E, Masson A, Moulut JC, et al. Comparison of direct (X-ray diffraction and infrared spectrophotometry) and indirect (infrared spectrophotometry) methods for the analysis of alpha-quartz in airborne dusts. *Ann Occup Hyg*. 2005; 49:661–71. [PubMed: 15972798]
- Lee T, Kim SW, Chisholm WP, et al. Performance of high flow rate samplers for respirable particle collection. *Ann Occup Hyg*. 2010; 54:697–709. [PubMed: 20660144]
- Lorberau CD, Abell MT. Methods used by the United States National Institute for occupational Safety and health to monitor crystalline silica. *Scand J Work Environ Health*. 1995; 2:35–8. [PubMed: 8929686]
- Lorberau CD, Carsey TP, Fischbach TJ, et al. Evaluation of direct-on-filter methods for the determination of respirable α -quartz. *Appl Occup Environ Hyg*. 1990; 5:27–35.
- Madsen, FAI; Rose, MC.; Cee, R. Review of quartz analytical methodologies: present and future needs. *Appl Occup Environ Hyg*. 1995; 10:991–1002.
- NIOSH. NIOSH hazard review: health effects of occupational exposure to respirable crystalline silica. Cincinnati, OH: National Institute for Occupational Safety and Health; 2002. Publication No. 2002-129
- NIOSH. NIOSH manual of analytical methods. 4th. Cincinnati, OH: National Institute for Occupational Safety and Health; 2003a. QUARTZ in coal mine dust, by IR (redeposition)
- NIOSH. NIOSH manual of analytical methods. 4th. Cincinnati, OH: National Institute for Occupational Safety and Health; 2003b. Silica, crystalline, by XRD (filter redeposition)
- Peters TM, Volkwein JC. Analysis of sampling line bias on respirable mass measurement. *Appl Occup Environ Hyg*. 2003; 18:458–65. [PubMed: 12746069]
- Pickard KJ, Walker RF, West NG. A comparison of X-ray diffraction and infrared spectrophotometric methods for the analysis of alpha quartz in airborne dust. *Ann Occup Hyg*. 1985; 29:149–67. [PubMed: 2998257]
- Shulman SA, Groff JH, Abell MT. Performance of laboratories measuring silica in the proficiency analytical testing program. *Am Ind Hyg Assoc J*. 1992; 53:49–56. [PubMed: 1317092]
- Shulman SA, Groff JH, Schlecht PC, et al. Performance of laboratories analyzing organic solvents in the proficiency analytical testing program. *Am Ind Hyg Assoc J*. 1996; 57:295–303.
- Stacey P. Analytical performance criteria—measurements of silica in air: reliability at new and proposed occupational exposure limits. *J Occup Environ Hyg*. 2007; 4:D1–4. [PubMed: 17162473]
- Stacey, P.; Thorpe, A. Testing of high flow rate respirable samplers to assess the technical feasibility of measuring 0.05 mg m^{-3} respirable crystalline silica. Buxton, UK: Health and Safety laboratory; 2009.
- Stacey P, Tylee B, Bard D, et al. The performance of laboratories analysing alpha-quartz in the Workplace Analysis Scheme for Proficiency (WASP). *Ann Occup Hyg*. 2003; 47:269–77. [PubMed: 12765867]
- Verma DK, Sebestyen A, Julian JA, et al. A comparison of two methods of sampling and analysis for free crystalline silica α -quartz. *Appl Occup Environ Hyg*. 1992; 7:758–63.
- Virji MA, Bello D, Woskie SR, et al. Analysis of quartz by FT-IR in air samples of construction dust. *Appl Occup Environ Hyg*. 2002; 17:165–75. [PubMed: 11871753]
- Volkwein, JC.; Vinson, RP.; McWilliams, LJ., et al. Performance of a new personal respirable dust monitor for mine use Report of Investigations 9663. Pittsburgh, PA: Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health; 2004.

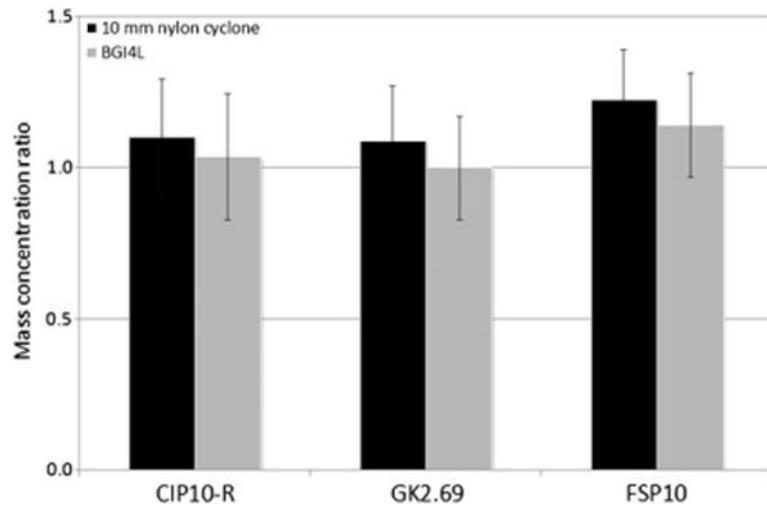


Fig. 1. Average and standard deviation of mass concentration ratios of high-flow rate samplers (CIP10-R, GK2.69, and FSP10) to low-flow rate samplers (10-mm nylon and BGI4L cyclones) when samplers were exposed to Coal Dusts A and B.

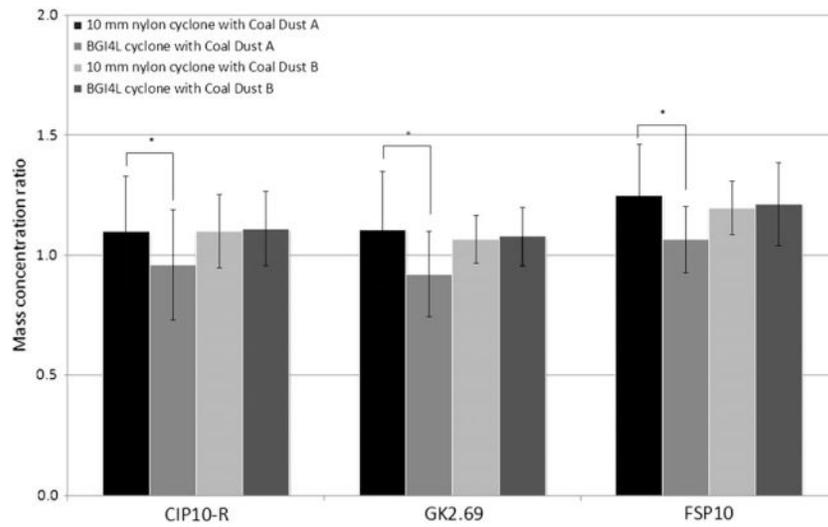


Fig. 2. Average and standard deviation of mass concentration ratios between high- and low-flow rate samplers when separated by Coal Dusts A and B. *Significantly different ($P < 0.05$).

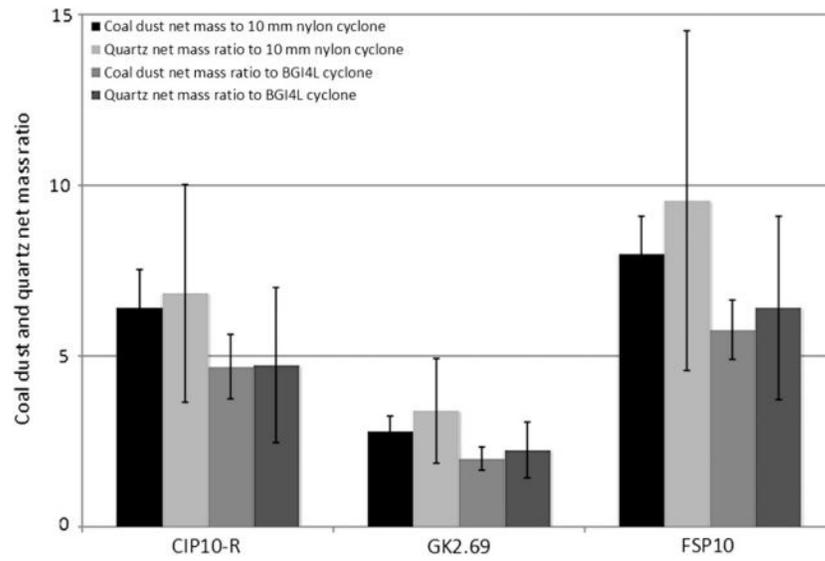


Fig. 3. Average and standard deviation of coal dust and quartz net mass ratios of high-flow rate samplers to low-flow rate samplers when the samplers were exposed to the Coal Dusts A and B.

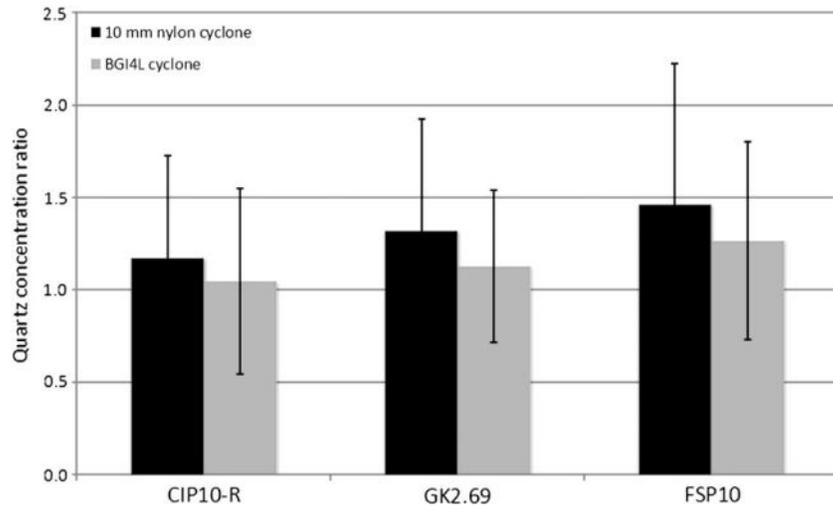


Fig. 4. Average and standard deviation of quartz concentration ratios of high-flow rate samplers (CIP10-R, GK2.69, and FSP10) to low-flow rate samplers (10-mm nylon and BGI4L cyclones) when samplers were exposed to Coal Dusts A and B.

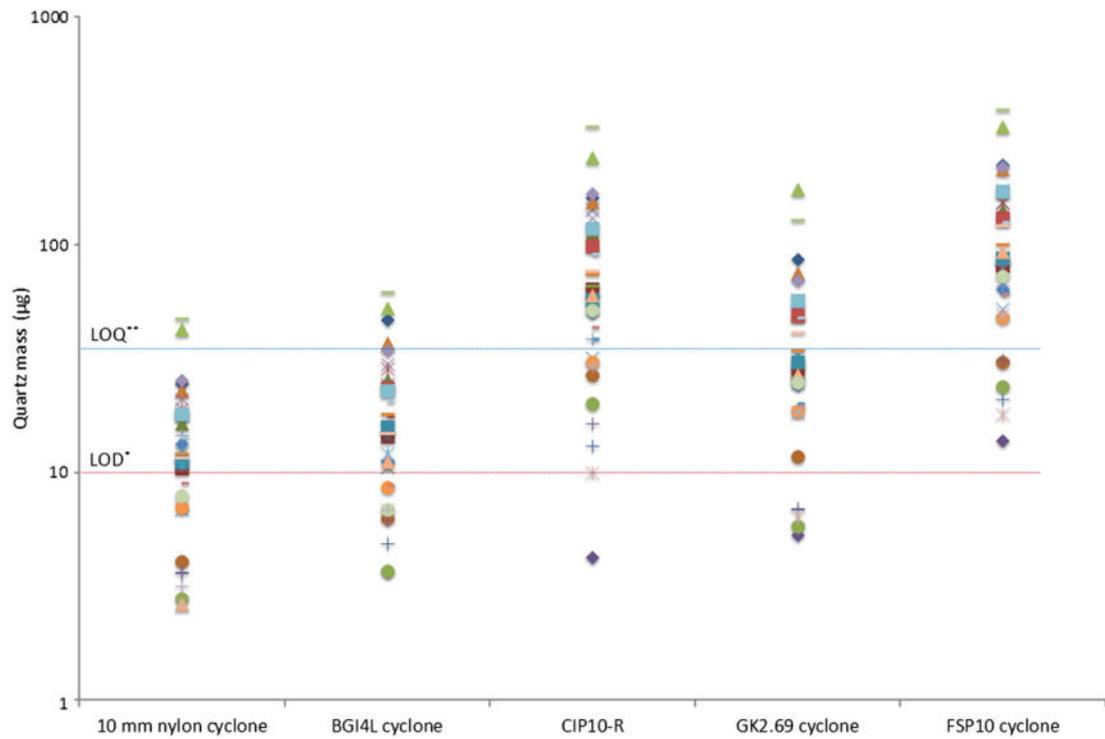


Fig. 5. Scatter plot of quartz mass collected with the 10-mm nylon, BGI4L, CIP10-R, GK2.69, and FSP10 samplers with LOD (10 µg) and LOQ (33 µg) of FTIR when the samplers were exposed to the Coal Dusts A and B ($n = 36$ for each samplers). *LOD from NMAM 7603, **LOQ(LOD \times 3.3) from NMAM 7603.

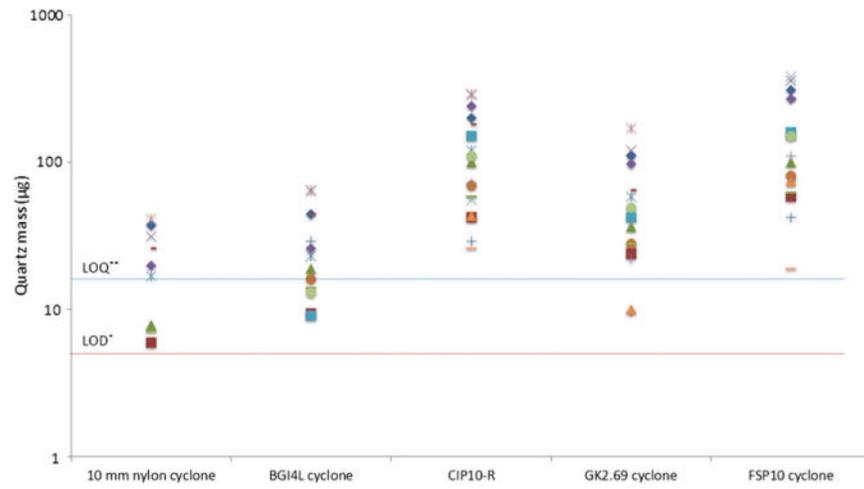


Fig. 6. Scatter plot of quartz mass collected with the 10-mm nylon, BGI4L, CIP10-R, GK2.69, and FSP10 samplers with LOD (5.5 µg) and LOQ (18.8 µg) of XRD when the samplers were exposed to the Coal Dusts A and B ($n = 18$ for each samplers). *LOD from NMAM 7500. **LOQ($\text{LOD} \times 3.3$) from NMAM 7500.

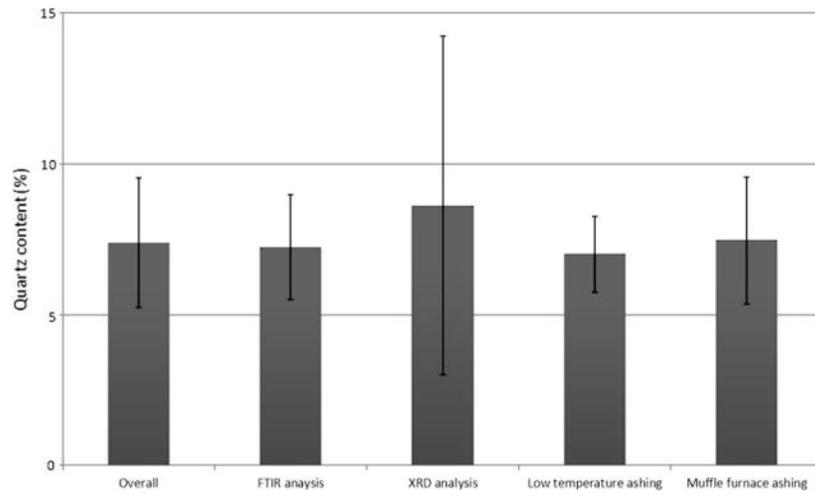


Fig. 7. Average and standard deviation of quartz content (%) in Coal Dusts A and B.

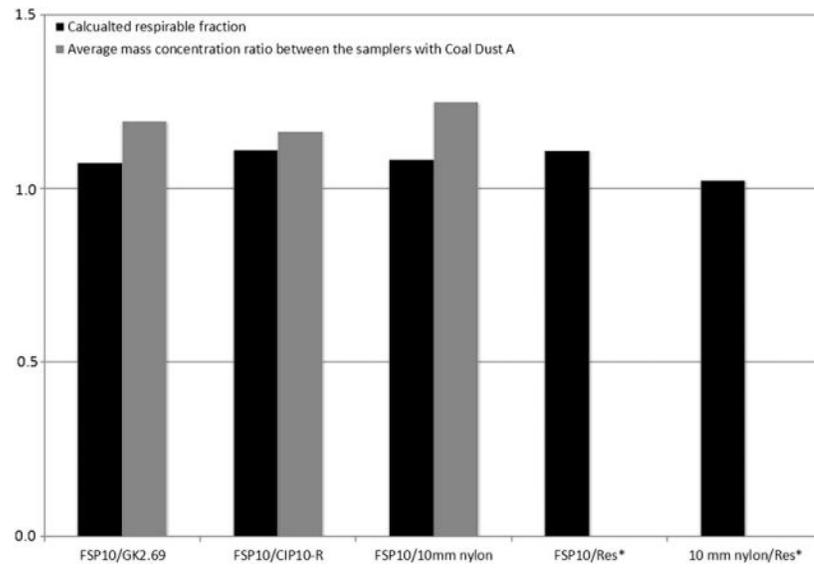
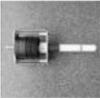
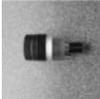


Fig. 8. Comparison calculated respirable fraction and average mass concentration ratio between the samplers with Coal Dust A. *Res is ISO respirable convention.

Table 1

Comparison of high- and low-flow rate samplers.

Samplers	Flow rate (1 min ⁻¹)	Sampling media	Sampling principle	Pump	Sampling hours for half of TLV**
 10 mm nylon cyclone	1.7	PVC filter (37 mm, 5µm pore size)	Cyclone size selection	SKC PCXR-4	7.8
 BG14L cyclone	2.2	PVC filter (37 mm, 5µm pore size)	Cyclone size selection	SKC PCXR-4	6.1
 CIP10-R	10	Polyurethane foam filter	Impaction and selective filtration	–	1.3
 GK2.69	4.2 (4.4)*	PVC filter (37 mm, 5µm pore size)	Cyclone size selection	SKC Legacy	3.0
 FSP10	10 (11.2)*	PVC filter (37 mm, 5µm pore size)	Cyclone size selection	SG10-2	1.2

* Adjusted flow rate to minimize the bias against ACGIH/CEN/ISO respirable convention and these were employed for this study.

** Number of hours required to obtain a sample at half of the TLV assuming that each sampler collects 10 µg of quartz.

Table 2

A summary of collected coal dust samples.

Quartz analysis method	FTIR		XRD
	Low temperature	Muffle furnace	
Organic material elimination methods			THF*
Sample number (<i>n</i>)	90	90	90

* Tetrahydrofuran

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Table 3

Linear regression analysis of mass concentration of Coal Dusts A (MMAD \approx 4.48 μ m) and B (MMAD \approx 2.33 μ m).

Samplers	Slope	Regression coefficient (R^2)
Higgins–Dewell/10-mm nylon	$y = 1.016 x$	0.941
CIP1y0-R/10-mm nylon	$y = 1.023 x$	0.959
GK2.69/10-mm nylon	$y = 1.059 x$	0.957
FSP10/10-mm nylon	$y = 1.187 x^a$	0.969
CIP10-R/BGI4L	$y = 0.964 x$	0.934
GK2.69/BGI4L	$y = 1.019 x$	0.971
FSP10/BGI4L	$y = 1.136 x^a$	0.973

^aSignificantly different from the unity relationship ($y = x$).