Effect of the Quartz Particle Size on XRD Quantifications and Its Implications for Field Collected Samples

Ching-Hwa Chen1, Jhy-Charm Soo2, Li-Hao Young2, Trong-Nen Wu2, Chungsik Yoon3, Chane-Yu Lai4, Perng-JyTsai1,2*

1 Department of Environmental and Occupational Health, Medical College, National Cheng Kung University, 138, Sheng-Li Rd., Tainan 70428, Taiwan
2 Department of Occupational Safety and Health, College of Public Health, China Medical University and Hospital, 91, Hsueh-Shih Rd, Taichung 40402, Taiwan
3 Institute of Health and Environment, School of Public Health, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 131-742, Korea
4 Department of Occupational Medicine, Chung Shan Medical University Hospital, 110, Sec.1, Jianguo N. Rd., Taichung City 40201, Taiwan

ABSTRACT

The aims of the present study were to assess the effect of the quartz particle size on XRD quantifications, and use it to develop models for correcting the measured quartz concentrations of samples collected from the field. Seven nearly monodispersed pure quartz dusts, with mass median aerodynamic diameters (MMAD) ranging from 0.70 to 10.84 µm, were prepared by a liquid sedimentation device, and their unit XRD intensities (UI) were measured using the NIOSH Method 7500. The results show that UI increases (from 0.63 to 1.14) along with the rise in MMAD of the pure quartz dust. To examine the impact of the above results on quantifying field collected samples, both total dust and respirable dust samplings were conducted at seven different workplace environments. The results show that the quartz particles contained in all collected total dust samples (MMAD = 5.18–16.7 µm, GSD = 2.08–2.88) were coarser in their particle sizes than that of the reference quartz standard (NIST-SRM 1878; MMAD = 2.16 µm, GSD = 1.55), and the measured total quartz particle concentrations (Cm) were 16.6–22.5% lower than the corresponding true concentrations (Ct). However, for respirable dust samples (MMAD = 1.37–3.95 µm, GSD = 1.978–2.87), since collected quartz particle sizes could be either finer or coarser than that of the reference standard, both underestimation and overestimation were found in the present study (Cm/Ct = 0.881–1.09). To correct the measured concentrations of field collected samples, correcting models were developed based on the MMADs of the collected quartz particle samples and their corresponding UIs. This study yields correcting factors for the respirable fraction (CRf) as CRf = 1.50 – 0.67 × [1 – exp(–0.69 × MMAD)] (R² = 0.996, n = 7). However, the obtained CRf should be used with caution if the collected samples were found with quartz particle sizes falling outside the size range of the present study.

Keywords: Quartz; Particle size distribution; X-ray diffraction; Exposure assessment.

INTRODUCTION

To date, both the NIOSH 7500 X-ray diffraction (XRD) method (NIOSH, 2003) and the NIOSH 7602 infrared (IR) spectrophotometer method (NIOSH, 1994) have been widely used for quantifying collected free crystalline silica (including quartz, tridymite, and cristobalite) filter samples.

In principle, the former is considered to be better than the latter due to its higher precision and accuracy (William, 1999). However, the accuracy associated with using XRD in quantification could be affected by the particle size of the crystalline silica containing in the collected sample. Many researchers have found that the measured XRD intensities increase with the increase in quartz particle sizes (Bhaskar et al., 1994; Yabuta and Ohta, 2003). However, it should be noted that the metrics used for describing the quartz particle size in the above studies were inconsistent. For example, the equivalent volume diameter (dv) was used by Bhaskar et al. (1994), and the aerodynamic diameter (dae) was adopted by Yabuta and Ohta (2003). Therefore,
developing a detailed numerical model for describing the relationship between the measured XRD intensities and the corresponding quartz particle sizes, by using the metric related to human exposure, would be of importance to the environmental health science field for conducting exposure assessments. In addition, it is known that particle sizes of a free crystalline silica reference standard used for XRD quantifications are poly-dispersed, and would have intrinsic differences in particle size distribution from those field collected samples. Therefore, it can be expected that quartz particle samples with various size distributions, though their true concentration are the same, would result in different measured concentrations even the same reference standard was used in the XRD analysis process (Kauffer et al., 2002; Chisholm, 2005; Stacey et al., 2009). To date, the effect associated the use of a reference standard on the quantification of field collected samples has never been assessed. In addition, the establishment of a suitable method for converting the measured concentration to true concentration would be of importance for conducting exposure assessment.

The first aim of this study is set out to numerically assess the effect associated with the particle size of crystalline silica on its measured XRD intensity. For illustration, only quartz was studied in the present study because it is the one most encountered in the environmental health science field among all crystalline silica types (Shih et al., 2008). The metric of the aerodynamic diameter ($d_{ae}$), which has been recognized as the one most related to human exposure to micrometer particles, was adopted in the present study (Vincent, 2007). To date, the NIST-SRM 1878 (MMAD = 2.16 µm, GSD = 1.55; National Institute of Standards and Technology, Gaithersburg, USA), as recommended by Verma and Shaw (Verma and Shaw, 2001), has been widely used as the reference standard for quartz quantifications. Therefore, the effect associated the use of it on quantifying field collected quartz samples was also investigated. Finally, nonlinear regression models were developed to correct the quantitative results for field collected samples while the NIST-SRM 1878 was used as the reference standard. The results obtained from the present study would be beneficial to the environmental health science field for accurately evaluating human quartz exposures.

**MATERIALS AND METHODS**

**Preparation of Pure Quartz Dust with Various Particle Sizes**

The quartz dust with a purity of ~99.0% and equivalent volume diameter ($d_v$) of ~15.1 µm ($d_{90\%} = ~39$ µm) (Pei Long Enterprise Co., Ltd., Changhua, Taiwan) was used for preparing pure quartz dust samples with various quartz particle sizes. The quartz dust was pretreated with phosphoric acid for 2 hr to remove metal impurities. Metals containing in pretreated quartz dust were analyzed per the NIOSH 7300 method using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, JY 2000, HORIBA Jobin Yvon, Longjumeau, France). A total of 22 metal elements were analyzed with the method of detection limits (MDLs) ranging from $2.01 \times 10^{-3}$ to $10.7 \times 10^{-3}$ mg.

To separate quartz dust into various particle sizes in $d_{ae}$, a 10 g of pretreated pure quartz dust was placed into a liquid sedimentation device (Fig. 1). Before the separation process, distilled water was added into the device until the water level reached 10 cm, and then ultrasonic shaking was conducted for 10 min to keep the pretreated pure quartz dust suspending in the water. The separation of particles was conducted via several repeated sedimentation processes with various specified settling times ($t$), which were determined according to Stokes’ law. The equation for the determination of the terminal settling velocity ($v_t$) of particles is:

$$v_t = \frac{4}{3} \pi \frac{d^2}{18} \left( \frac{1}{\rho_s} - \frac{1}{\rho} \right) g$$

where $d$ is the particle diameter, $\rho_s$ is the particle density, $\rho$ is the fluid density, and $g$ is the gravitational acceleration.

![Fig. 1. The schematic of the liquid sedimentation device used in the present study.](image-url)
of the $t$ (sec) can be expressed as the following:

$$
 t = \frac{18 \times \eta \times 10^6}{\left(\rho_p - \rho_0\right) \times G \times (d'_{ae})^2} \times L
$$

where $\eta$ is the viscosity coefficient of the medium (i.e., water) at $20^\circ C$ ($= 1.01 \times 10^{-3}$ g/cm·s), $\rho_p$ is the density of the quartz dust ($= 2.65$ g/cm$^3$), $\rho_0$ is the density of water ($= 0.998$ g/cm$^3$ at $20^\circ C$), $G$ is the gravitational acceleration ($= 980$ cm/s$^2$), $d'_{ae}$ is the targeted particle size to be separated in aerodynamic diameter, and $L$ is the settling distance for the pure quartz dust ($=$ height of the water level of the device $= 10$ cm). This study yielded $t$ specified for quartz dust with $d'_{ae}$ values of $0.8$, $1.2$, $2.0$, $3.0$, $6.0$, $9.0$, and $12.0$ µm were $48$ hr $44$ min, $21$ hr $39$ min, $7$ hr $47$ min, $3$ hr $27$ min, $52$ min, $23$ min $6$s, and $13$ min, respectively.

The particle size separation process began with a settling time of $48$ hr $44$ min. During the sedimentation process, the sink lid was placed on the sink top to prevent from the error associated with the deposition of pretreated pure quartz dusts directly onto the sink. After the first sedimentation process, the water suspension was collected by removing the sink lid from the sink top and opening the drainage valve simultaneously. The collected water was filtered by a mixed cellulose ester (MCE) filter with a $0.8$-µm pore size. The filter was then placed in a furnace for $2$ hr at $600^\circ C$ to obtain the separated pure quartz dust with $d''_{ae} < 0.8$ µm. The same process was repeated for the other six designated settling times in order to separate pure quartz dust with $d''_{ae}$ of $0.8$–$1.2$, $1.2$–$2.0$, $2.0$–$3.0$, $3.0$–$6.0$, $6.0$–$9.0$, and $9.0$–$12.0$ µm, respectively. A similar device had been used in one study conducted for the same purpose (Yabuta and Ohta, 2003).

### Determining the True Particle Sizes of the Separated Pure Quartz Dust

Separated pure quartz dusts with $d''_{ae}$ of $< 0.8$, $0.8$–$1.2$, $1.2$–$2.0$, $2.0$–$3.0$, and $3.0$–$6.0$ µm were further measured using a transmission electron microscope (TEM, JEM-1400, JEOL Co., Ltd, Tokyo, Japan) to determine their projected area diameters ($d_p$, µm). For those separated pure quartz dusts with $d''_{ae}$ of $6.0$–$9.0$, and $9.0$–$12.0$ µm, their $d_p$ were determined using a scanning electron microscope (SEM, S4100, Hitachi, Tokyo, Japan). Here, $0.01$ mg of each separated pure quartz dust was first mixed with $5$ mL of distilled water and then had a ultrasonic shaking for $10$ min. For TEM analyses, $10$ µL of suspension was placed on a slide and dried. For SEM observations, $10$ µL of suspension was placed on a conductive carbon tape, dried, and gilded. For each separated pure quartz dust, ~$15$ TEM (or SEM) images were obtained. ~$100$ particles were measured and their $d_p$ values were used to determine the true aerodynamic diameter ($d''_{ae}$, µm) using equation of the following:

$$
d''_{ae} = \frac{d_p}{S_p \times \left(\frac{\rho_p S_v}{\rho_v}\right)}
$$

where $S_o$ is the dynamic shape factor of the pure quartz dust ($= 1.36$) and $S_v$ is the volume shape factor of quartz ($= 1.25$) (Davies, 1979). The obtained $d''_{ae}$ values were used to determine the number-based particle size distribution (including the number median aerodynamic diameter (NMAD) and the geometric standard deviation (GSD)) of the separated pure quartz dust. For any given particle size distribution, it is known that both of its number-based and mass-based size distribution share the same GSD (Baron and Willeke, 2001). According to the Hatch-Choate equation, the mass median aerodynamic diameter (MMAD) can be determined by the following (Vincent, 1995):

$$
\text{MMAD} = \text{NMAD} \times \exp(3 \times \ln^2 \text{GSD})
$$

### XRD Analyses of the Separated Pure Quartz Dusts

The unit XRD intensity (UI, XRD intensity/µg) for each separated pure quartz dust was determined per NIOSH Method 7500 through XRD analysis (NIOSH, 2003). For XRD analysis, scanning was performed in a $20$ range of $15^\circ$ to $65^\circ$. The scanning speed was $1^\circ$/min and the step size was $0.01^\circ$. The calibration curve for all separated pure quartz dusts covered the range of $25$ to $1000$ µg with $R^2$ of $\sim 0.998$. By analyzing three samples for each separated pure quartz dust with a given concentration, the accuracy and precision were found to be $\sim 3.3$% and $\sim 4.0$% respectively. By analyzing $7$ samples on different days, the instrument stability was found to be $\sim 10$%. This study yielded a MDL of $\sim 0.024$ mg from all separated pure quartz dusts for quantifying their quartz content.

In the present study, a nonlinear regression equation was used to describe the relationship between UI and its corresponding $d''_{ae}$ and the effect associated with the quartz particle size on XRD quantification was assessed.

### Field Sampling and Sample Analyses

In this study, field samplings were conducted at three sampling workplaces in an iron and steel plant (including the air stove, coke oven/roof, and coke oven/sidewalk) during the stove repairing period, and four work stages inside a municipal waste incinerator during its annual maintenance period (including the stove repairing, refractory material repairing, scaffold removing, and stove cleaning).

For each selected workplace (or work stage), three cascade impactors (Marple 298 cascade impactor, Thermo Andersen Inc., Smyrna, GA, USA) were used for conducting particle-size-segregating samplings with a sampling flow rate specified at $2.0$ L/min. The cascade impactor consists of eight impaction stages ($d_{50,\text{imp}} = 0.52$, $0.96$, $1.55$, $3.5$, $6.0$, $9.8$, $14.8$, and $21.3$ µm, respectively) and a back-up filter (34-mm PVC filter with $5.0$-µm pore size; Omega Specialty Instrument, Co., Houston, USA). For sample collected on the $i$th impaction stage, its measured XRD intensity ($I_i$) was determined per NIOSH Method 7500 as described in the previous section (NIOSH, 2003).

### Determining True Quartz Concentrations for Field Collected Samples

For sample collected on the $i$th impaction stage, its true
quartz concentration \((C_n)\) could be determined by its measured XRD intensity \((I_i)\) and the corresponding unit intensities \((U_{NI})\). Here, \(U_{NI} \) can be calculated based on \(d_{505}\%\) of the \(i^{th}\) impaction stage and the nonlinear regression equation, which was used to describe the relationship between \(U_i\) and its corresponding \(d''_{ae}\) (see section 2.3). The true quartz concentration \((C_i)\) could then be determined by the following:

\[
C_i = I_i / U_{ci}
\]

The resultant \(C_i\) of the eight impaction stages were used to describe the true particle size distribution of the quartz content found in the workplace atmosphere. In addition, by summing up the concentrations of the eight impaction stages and the result was regarded as the total true quartz concentrations \((C_t)\), the concentration of all quartz particles containing in the atmosphere of the selected workplace). Here, \(C_t\) can be determined by the following:

\[
C_t = \sum_{i=1}^{8} C_i = \sum_{i=1}^{8} I_i / U_{ci}
\]  

(5)

In this study, the concentration of the respirable fraction \((CR_i)\) for sample collected on the \(i^{th}\) impaction stage can be obtained by the collected concentration \((C_i)\) and the corresponding respirable fraction \((R_i)\) of dusts collected on the stage. Here, \(R_i\) can be obtained from the criteria currently adopted by the International Standards Organization (ISO), Comité Européen Normalization (CEN), and American Conference for Governmental Industrial Hygienists (ACGIH) (ACGIH, 1995–1996; CEN, 1992; ISO; 1992). In this study, \(CR_i\) can be determined by the following:

\[
CR_i = C_i \times R_i
\]

(6)

Again, the resultant \(CR_i\) of the eight stages were used to describe the particle size distribution of the respirable quartz content found in the workplace atmosphere. Through the integration of the respirable fraction of the eight impaction stages, the true respirable quartz concentration \((CR_t)\) can then be determined by the following:

\[
CR_t = \sum_{i=1}^{8} CR_i = \sum_{i=1}^{8} C_i \times R_i = \sum_{i=1}^{8} I_i / U_{NI} \times R_i
\]

(7)

### Determining Measured Quartz Concentrations and Their Corresponding Conversion Factors for Field Collected Samples

To date, the NIST-SRM 1878 has been widely used as the reference standard for the quantification of field collected quartz samples. In this study, the unit intensity for NIST-SRM 1878 \((U_{NI})\) was also determined per NIOSH Method 7500 through XRD analysis (NIOSH, 2003). This study yielded \(U_{NI}\) as 0.840 XRD intensity/µg. By reference to the standard of NIST-SRM 1878, the measured quartz concentration for sample collected on the \(i^{th}\) impaction stage \((C_{mi})\) can be determined by the following:

\[
C_{mi} = I_i / U_{NI}
\]

(8)

The total measured quartz concentrations \((C_m)\) can be determined by adding up the concentrations of the eight impaction stages as the following:

\[
C_m = \sum_{i=1}^{8} C_{mi} = \sum_{i=1}^{8} I_i / U_{NI}
\]

(9)

In the present study, the conversion factor \((C_f)\) was defined as the following:

\[
C_f = C_i / C_m
\]

(10)

In principle, if \(C_f\) could be obtained for samples collected from a given size distributions, it would be useful for converting \(C_m\) into \(C_t\) in the field. In this study, a nonlinear regression model was developed for describing \(C_f\) and samples with various size distributions for the above purpose.

By taking the respirable fraction into account, the measured respirable quartz concentration for sample collected on the \(i^{th}\) impaction stage \((CR_{mi})\) can be determined by the following:

\[
CR_{mi} = C_{mi} \times R_i
\]

(11)

Using the \(CR_{mi}\) of the eight impaction stages, the particle size distribution of the respirable quartz can be determined (in terms of its MMAD and GSD). Finally, the summation of \(CR_{mi}\) of the eight impaction stages is calculated as the total measured respirable quartz concentration \((CR_m)\) by the following:

\[
CR_m = \sum_{i=1}^{8} CR_{mi} = \sum_{i=1}^{8} C_{mi} \times R_i = \sum_{i=1}^{8} I_i / U_{NI} \times R_i
\]

(12)

Again, the conversion factor for the respirable fraction \((CR_f)\) was defined as the following:

\[
CR_f = CR_m / CR_m
\]

(13)

For converting \(CR_m\) into \(CR_t\) in the field, a nonlinear regression model was developed in the present study for describing \(C_f\) and samples with various size distributions.

### RESULTS AND DISCUSSION

#### Separated Pure Quartz Dusts

Table 1 shows metal contents found in pure quartz dusts after being pretreated with phosphoric acid. Among 22 analyzed metal elements, only 7 (Cd, Co, Cr, Cu, Ni, Pb, and

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Table 1. Metal contents containing in the pretreated pure quartz dust (n = 3).

| Metal | Mean ± SD (% by weight) |
|-------|-------------------------|
| Cd    | 5.10 × 10⁻³ ± 3.20 × 10⁻³ |
| Co    | 9.10 × 10⁻³ ± 6.20 × 10⁻³ |
| Cr    | 1.40 × 10⁻² ± 5.10 × 10⁻³ |
| Cu    | 2.10 × 10⁻² ± 2.20 × 10⁻² |
| Ni    | 4.60 × 10⁻³ ± 4.00 × 10⁻³ |
| Pb    | 8.70 × 10⁻² ± 3.30 × 10⁻² |
| Ti    | 7.00 × 10⁻¹ ± 7.9 × 10⁻² |
| Total | 8.40 × 10⁻¹ ± 6.3 × 10⁻² |

Tellurium (Te) were detectable and in total accounted only for ~0.84% of the weight. In the present study, ~10 g of pretreated pure quartz dust was put into a liquid sedimentation device (Fig. 1) in order to classify it into various targeted particle sizes (\(d'_{ae}\)).

The images for those separated pure quartz dust with \(d'_{ae}\) < 0.8, 0.8–1.2, 1.2–2.0, 2.0–3.0, and 3.0–6.0 µm were measured using a TEM (JEM-1400, JEOL Co., Ltd, Tokyo, Japan) to determine their projected area diameters (\(d_p\)). For those with \(d'_{ae}\) of 6.0–9.0 and 9.0–12.0 µm, their \(d_p\) were determined according to images measured by an SEM (S4100, Hitachi, Tokyo, Japan). For illustration, Fig. 2 shows the images of separated pure quartz dusts with \(d'_{ae}\) of 2–3 µm and 6–9 µm obtained from TEM and SEM, respectively. In this study, the true particle size (\(d''_{ae}\)) for each separated pure quartz dust was determined by applying the corresponding \(d_p\) obtained from TEM (or SEM) images to Eq. (2). The resultant \(d''_{ae}\) values were used to determine the number-based particle size distribution (including the number median aerodynamic diameter (NMAD) and the geometric standard deviation (GSD)). Since both number-based and mass-based size distribution share the same GSD, the Hatch-Choate equation was used to convert NMAD to the mass median aerodynamic diameter (MMAD) according to Eq. (3).

Table 2 shows the resultant true particle size distribution (shown as its MMAD ± GSD) of \(d''_{ae}\) for each separated pure quartz dust. Here, \(d''_{ae}\) of < 0.8, 0.8–1.2, 1.2–2.0, 2.0–3.0, 3.0–6.0, 6.0–9.0, and 9.0–12.0 µm were found with \(d''_{ae}\) of 0.700 µm ± 1.66, 1.05 µm ± 1.81, 1.94 µm ± 1.53, 2.76 µm ± 1.55, 5.25 µm ± 1.44, 8.51 µm ± 1.39, and 10.9 µm ± 1.50, respectively. All resultant GSD were found around 1.50 indicating that each separated pure quartz dust was quite mono-dispersed. Therefore, the MMAD was considered adequately to characterize the particle size for each separated pure quartz dust.

Effect of Quartz Particle Size on Measured XRD Intensities

Table 2 also shows the obtained UI (XRD intensity/µg) for each separated pure quartz dust. Fig. 3 shows the relationship between UI and MMAD obtained from the seven separated pure quartz dust samples. This study yielded a nonlinear regression equation for the above relationship as:

\[
UI (\text{MMAD}) = 0.498 + 0.681[1 – \exp(–0.318 + \text{MMAD})] \\
\left( R^2 = 0.996, n = 7 \right)
\]

Obviously, our results suggest that the value of UI is increased as the increase in MMAD. The above trend is consistent with those reported by previous research works (Bhaskar et al., 1994; Yabuta and Ohta, 2003). In addition, the results also indicate that UI values are increased sharply for those MMAD from 0.700 to 5.25 µm, but slowly for those from 5.25 to 10.8 µm. Here, it should be noted that the UI for MMAD of 0.700 µm (i.e., 0.63 ± 0.08 XRD intensity/µg) is only ~0.553 times in magnitude as that of 10.84 µm (i.e., 1.14 ± 0.02 XRD intensity/µg). Therefore, if quartz dust samples with the above two MMAD were found with the same XRD intensity, the quantification result for the former would be ~1.81 times in magnitude higher than that of the latter. The above result further indicates the significant effect of the quartz particle size on XRD quantification results.

True Quartz Concentrations and Their Conversion Factors for the Field Collected Samples

Table 3 shows the unit intensities (\(U_{I,a}\)) for samples collected on the \(i^{th}\) impaction stages of the cascade impactor used in the present study. Here, \(U_{I,a}\) was calculated based on \(d_{50\%}\) of the \(i^{th}\) impaction stage and the obtained nonlinear regression model (see Eq. (14)). For each selected

![Fig. 2](image-url)
Table 2. Targeted particle sizes ($d'_{ae}$), their corresponding true particle sizes ($d''_{ae}$) and mean unit intensities (UI) of the seven separated pure quartz dusts.

| Targeted particle sizes ($d'_{ae}; \mu m$) | True particle size ($d''_{ae}; \mu m$) | MMAD ± GSD | Mean ± SD |
|------------------------------------------|---------------------------------------|------------|----------|
| < 0.8                                    | 0.700 ± 1.66                          | 0.63 ± 0.08|          |
| 0.8–1.2                                  | 1.05 ± 1.81                           | 0.68 ± 0.02|          |
| 1.2–2.0                                  | 1.94 ± 1.53                           | 0.80 ± 0.03|          |
| 2.0–3.0                                  | 2.76 ± 1.55                           | 0.88 ± 0.02|          |
| 3.0–6.0                                  | 5.25 ± 1.44                           | 1.07 ± 0.04|          |
| 5.0–9.0                                  | 8.51 ± 1.39                           | 1.12 ± 0.03|          |
| 9.0–12.0                                 | 10.84 ± 1.50                          | 1.14 ± 0.02|          |

Fig. 3. The relationship between unit intensity (UI) and MMAD of the true quartz particle size.

Table 3. The calculated unit intensities ($U_{lec}$) for $i^{th}$ stage Marple cascade impactor and respirable fraction ($R_i$).

| Impaction stage | $d_{50\%}$ of Marple cascade impactor ($\mu m$) | $U_{lec}$ (XRD intensity/µg) | $R_i$ |
|-----------------|-----------------------------------------------|----------------------------|-------|
| 1               | 21.3                                         | 1.18*                      | 0.000 |
| 2               | 14.8                                         | 1.17*                      | 0.000 |
| 3               | 9.8                                          | 1.15                       | 0.008 |
| 4               | 6                                            | 1.08                       | 0.163 |
| 5               | 3.5                                          | 0.958                      | 0.624 |
| 6               | 1.55                                         | 0.766                      | 0.926 |
| 7               | 0.96                                         | 0.680                      | 0.972 |
| 8+filter        | 0.52                                         | 0.604                      | 1.000 |

* Values are extrapolated from Eq. (15).

field sampling site, the XRD intensity ($I_i$) for sample collected on the $i^{th}$ impaction stage of the cascade impactor was determined per NIOSH Method 7500 (NIOSH, 2003). Therefore, $C_{p}, C_i, C_{m}$, and $C_f$ could be determined by Eq. 4, 5, 8, and 9, respectively, and $C_f$ for converting $C_m$ to $C_i$ could be determined by Eq. (10). In this study, only quartz particle size distributions and their corresponding $C_{p}, C_m$, and conversion factors ($C_f$) were shown in Table 4. For samples collected from the iron and steel plant, all obtained size distributions were found consistently with a unimodal form (Table 4). Through our field observation, we found that hammering was the main process associated with the generation of aerosols during the stove/oven repairing period. Since hammering could result in brittle fracture of the refractory materials, which has been known as the main mechanism associated with the emission of
coarse dusts with a unimodal form (Zhang et al., 1994; Bianchi et al., 1998; Soo et al., 2011). Therefore, the results obtained from the present study could be theoretically plausible. We also found that MMAD ± GSD obtained from the three selected workplaces of the air stove, coke oven/ sidewalk, and coke oven/roof were 5.18 µm ± 2.28, 8.53 µm ± 2.09, and 10.3 µm ± 2.20, respectively (Table 4). Based on our field investigation, we found that both alumina brick and alumina-magnesia brick were used as the refractory material for the workplace of the air stove because of their good heat transfer and storage characteristics. But for the coke oven, both sillimanite brick and silica brick were used as the refractory material for the corrosion and wear prevention purposes. Since the hardness of the involved refractory materials and the hammering strength were not measured in the present study, it might not be possible to explain the differences in particle size distributions among the three selected workplaces. Nevertheless, Ct obtained from the air stove (= 0.242 mg/m³) was much lower than that from coke oven workplaces (2.95 and 2.33 mg/m³ for the sidewalk and roof, respectively) (Table 4) which could be partly explained by the fact that both alumina brick and alumina-magnesia brick are known containing less quartz content than that of sillimanite brick and silica brick. A unimodal particle size distribution of quartz could also be found for samples collected from the four work stages inside a municipal waste incinerator during its annual maintenance period (Table 4). Since the hammering was adopted at both stove repairing, refractory material repairing stages, and hence the emission of coarse dusts with a unimodal form could be possible. Though at the scaffold removing stage no hammering was involved, the aerosols found in the atmosphere could be those generated from the above two work processes but still remained in the workplace atmosphere. As for the stove cleaning stage, the aerosols found in the atmosphere could be mainly due to the re-suspension of aerosols during the floor cleaning process. Therefore, the unimodal form could be explained by the above bulk agitation process. Table 4 also shows MMAD ± GSD of the unimodal quartz particle size distribution for the four selected work stages (= 15.1 µm ± 2.71, 16.7 µm ± 2.08, 15.8 µm ± 2.88, and 8.50 µm ± 2.25 for the stove repairing, refractory material repairing, scaffold removing, and stove cleaning, respectively). Here, the particle size of the latter was much finer than that of the former three could be due to the intrinsic differences in the involved aerosol generation mechanisms. On the other hand, the particle sizes of the former three were quite similar indicating that our previous inference could be possible (i.e., sharing the same aerosol generation process or generated aerosols). In this study, Ct for the above four work stages were found as 2.06, 1.25, 0.410, and 25.5 mg/m³, respectively (Table 4). Since both stove repairing and refractory material repairing involved in the demolition of refractory materials, and hence their concentrations were quite comparable. Because the aerosols found in the scaffold removing process could be mainly coming from those generated from the above two work processes but after sedimentation, it is not surprising to see that its concentration was much lower than that of

| Sampling plant          | Sampling workplace/stage | Particle size distributions of the collected quartz dusts (µm) | MMAD ± GSD (µm) | Ct (mg/m³) | Cm (mg/m³) | Cf (mg/m³) |
|------------------------|--------------------------|---------------------------------------------------------------|----------------|----------|-----------|------------|
| Iron and steel plant   | Air stove                | 5.18 ± 2.28                                                  | 0.242          | 0.290    | 0.834     | 0.834      |
|                        | Coke oven/Sidewalk       | 8.53 ± 2.09                                                  | 2.95           | 3.73     | 0.781     | 0.781      |
|                        | Coke oven/roof           | 10.3 ± 2.00                                                  | 2.33           | 2.99     | 0.775     | 0.775      |
|                        | Stove repairing          | 15.1 ± 2.71                                                  | 2.33           | 2.66     | 1.64      | 0.765      |
|                        | Refractory material repairing | 16.7 ± 2.08                                              | 2.06           | 1.64     | 0.775     | 0.775      |
|                        | Scaffold removing        | 15.8 ± 2.88                                                  | 1.25           | 1.64     | 0.529     | 0.792      |
| Municipal waste incinerator | Stove cleaning             | 8.50 ± 2.25                                                  | 25.5           | 0.410    | 0.529     | 0.792      |
the above two work processes. Finally, since the stove cleaning process was used to remove demolished refractory materials, its high concentration might be explained by its high agitation process.

Table 4 also shows the conversion factors \((C_n)\) for the selected seven workplaces/work stages. It is known that the value of UI is increased as in \(d''_{ae}\) increased (see Eq. (15)). Since the obtained particle size distributions (MMAD = 5.18–16.7 µm, GSD = 2.08–2.88) were consistently coarser than that of NIST-SRM 1878 (MMAD = 2.16 µm, GSD = 1.55), it is not so surprising to see that all resultant \(C_m\) values (0.29–32.2 mg/m³) were higher than their corresponding \(C_t\) values (0.242–25.535 mg/m³). As a result, the use of NIST-SRM 1878 as a reference standard for quantification of quartz samples would result in overestimation of field sample concentrations.

In the present study, the resultant GSD fell within the range of 2.08–2.88 indicating the variation of the quartz particle size distribution for the seven selected workplaces/work stages were quite similar. In order to properly convert \(C_m\) to \(C_t\) for samples collected from the field, therefore, a nonlinear regression equation was developed to relate MMAD and its corresponding \(C_f\) based on the results obtained from the seven selected workplaces/work stages. This study yielded the regression equation as (Fig. 4):

\[
C_f = 0.774 + 0.371 \times [1 – \exp(-0.355 \times \text{MMAD})]
\]

\((R^2 = 0.980, n = 7)\) (15)

Though particle size distributions obtained from the present study (MMAD = 5.18–16.7 µm, GSD = 2.08–2.88) might cover most particle size distributions which could be encountered in the field, caution should be taken for the use of the above equation if the obtained size distributions fell outside the above designated range.

### Respirable Quartz Concentrations and Their Conversion Factors for the Field Collected Samples

In this study, the respirable fraction \((R_i)\) of the \(i^{th}\) impaction stages for the cascade impactor used in the present study can be seen in Table 3 based on the criteria currently adopted by the ISO, CEN, and ACGIH (ACGIH, 1995–1996; CEN, 1992; ISO; 1992). By taking \(R_i\) into account, \(CR_{ti}, CR_t, CR_{mi}, CR_m,\) and \(CR_f\) were determined by Eqs. (6), (7), (11), (12), and (13), respectively. In this part of study, only the obtained particle size distributions of the respirable fraction and their corresponding \(CR_t, CR_m\) and \(CR_f\) were shown in Table 5.

For all selected workplaces/work stages, the obtained size distributions of the respirable quartz fraction (MMAD = 1.37–1.88 µm, GSD = 2.09–2.87) (Table 5) were finer than that of true total quartz particles (MMAD = 5.18–16.7 µm, GSD = 2.08–2.88) (Table 4). The above results are mainly because the respirable fraction is only a sub-fraction of the true total. But it should be noted that the obtained size distributions of the respirable fraction for the air stove (1.37 µm ± 2.09), stove cleaning (1.80 µm ± 2.87), and coke oven/side walk (1.88 µm ± 2.40) were finer than that of the reference standard of NIST-SRM 1878 (MMAD = 2.16 µm, GSD = 1.55). Therefore, their \(CR_t\) (0.062–1.65 mg/m³) were found to be higher than the corresponding \(CR_m\) (0.057–1.63 mg/m³). As a result, their \(CR_f\) (1.01–1.09) were consistently higher than unity. On the other hand, the obtained size distributions of the respirable fraction for the other four workplaces/work stages (MMAD = 2.68–3.95 µm, GSD = 1.97–2.32) were coarser than that of the reference standard of NIST-SRM 1878 (MMAD = 2.16 µm, GSD = 1.55). Therefore, their \(CR_t\) (0.035–0.154 mg/m³) were found to be lower than the corresponding \(CR_m\) (0.040–0.166 mg/m³), and hence the corresponding \(CR_f\) (0.866–0.928) were consistently lower than unity.

![Fig. 4. The relationship between the conversion factors \((C_f)\) and their corresponding MMADs of the true quartz dust for samples collected from the seven selected workplaces/work stages.](image-url)
In the present study, we found that all obtained GSDs of the respirable quartz fraction fell within the range of 1.97–2.87 indicating the variations in particle sizes of the collected respirable quartz particle samples from the seven selected workplaces/work stages were quite similar. Therefore, a nonlinear regression equation was developed by relating $CR_f$ to its corresponding MMAD based on the results obtained from the seven collected respirable quartz particle size distributions. This study yielded the regression equation as (Fig. 5):

$$CR_f = 1.50 - 0.67 \times [1 - \exp(-0.69 \times \text{MMAD})] \quad (R^2 = 0.996, \ n = 7) \quad (16)$$

In principle, particle size distributions of the respirable fraction obtained from the present study (MMAD = 1.37–3.95 µm, GSD = 1.97–2.87) would cover most of which could be encountered in the field. However, the use of the above equation for converting $CR_m$ to $CR_t$ in the field should be taken with caution if the obtained size distributions fell outside the above designated range.

CONCLUSION

In this study, we found that quite mono-dispersed pure quartz dusts can be obtained using the liquid sedimentation device developed by the present study. The developed nonlinear regression equation suggests that the value of UI is increased as the increase in MMAD of the separated pure quartz dust. According to field sampling results, the obtained dimensions of the quartz particles in all collected total dust samples were consistently coarser than that of the reference quartz standard. Therefore, all $C_m$ were higher than the corresponding $C_t$ and all resultant $C_f$ were less than unity. The established nonlinear regression equation of $C_f = 0.774 + 0.371 \times [1 - \exp(-0.355 \times \text{MMAD})]$ would provide a useful basis for converting $C_m$ to $C_t$ for all field collected samples in the future. For the seven field collected respirable dust samples, three and four of them were found with sizes of collected quartz particles finer and coarser than that of NIST-SRM 1878, respectively. Therefore, the $CR_f$ for the former three were higher than the corresponding $CR_m$, and the resultant $C_f$ were consistently lower than unity. To the contrary, the latter four were found with $CR_f$ higher than their corresponding $CR_m$ with $C_f$ consistently higher than unity. This study yielded a regression equation $CR_f = 1.50 - 0.67 \times [1 - \exp(-0.69 \times \text{MMAD})]$ for converting $CR_m$ to $CR_f$ for all collected field samples. However, the obtained converting factors should be the used with caution if collected samples were found with the quartz particle sizes fell outside the size range of the present study.

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Fig. 5. The relationship between the conversion factors ($CR_f$) and their corresponding MMADs of the respirable quartz for samples collected from the seven selected workplaces/work stages.

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