Quantitative Determination of Airborne Respirable Non-Fibrous α-Silicon Carbide by X-ray Powder Diffractometry

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Objectives: The purpose of the present investigation was to establish a method for the determination of airborne respirable non-fibrous silicon carbide (SiC). The main application is within the industrial production of SiC.

Methods: Due to the complex airborne aerosol mixture of crystalline compounds in the SiC industry, X-ray powder diffractometry was selected as the most appropriate method. Without any international standard material for the respirable fraction of non-fibrous SiC, pure and suitable products from three SiC plants in Norway were selected. These products have a median particle diameter in the range 4.4–5.1 µm. The method is based on thin sample technique, with the dust deposited on a polycarbonate filter. Absorption correction is done by standard procedures with the use of a silver filter, situated below the polycarbonate filter.

Results: The diffraction line used for quantitative determination was selected carefully. This was done to avoid interferences from quartz, cristobalite, and graphite, which all are airborne components present in the atmosphere during the industrial process. The instrumental limit of detection for the method is 12 µg.

Conclusions: This method has been used to determine airborne non-fibrous SiC in a comprehensive ongoing project in the Norwegian SiC industry for further epidemiological studies. The method is fully applicable for compliance work.

Keywords: airborne aerosols; industrial production; non-fibrous silicon carbide; quantitative determination; X-ray diffractometry

INTRODUCTION

Romundstad et al. (2001, 2002) have recently reported an increased risk of lung cancer, other lung diseases, and non-malignant mortality among workers in the Norwegian silicon carbide (SiC) industry. The workers in this industry are exposed to a complex mixture of particulates and gases. The airborne aerosol consists of quartz, cristobalite, SiC fibres, non-fibrous SiC dust, polycyclic aromatic hydrocarbons, graphite, and other carbonaceous dust as described by Bye (1983), Bye et al. (1985), Dufresne et al. (1987a,b), Osterman et al. (1989), Scansetti et al. (1992), Gunnaes et al. (2005), Skogstad et al. (2006), and Føreland et al. (2008). Romundstad et al. (2001) showed that an increased risk of lung cancer could be associated with increased cumulative exposure to total dust. However, they could not identify any causative specific chemical agent for the increased risk of lung diseases.

The SiC fibre was the suspected agent for the increased cancer risk, possibly besides or in combination with crystalline silica (Romundstad et al., 2001; IARC, 1987). However, the exposure matrix used in the epidemiological study showed a considerable covariance between several airborne chemical constituents. A more
detailed and comprehensive job-exposure matrix (JEM) might hopefully give an improved model to compare health indicators with a retrospective exposure description. An important part of this improvement would be a direct determination of non-fibrous SiC.

A mixture of quartz sand and petrol coke produces SiC in open electrical resistance furnaces. The temperature is 2200–2500°C, applying the Acheson method (Smith et al., 1984). A core of graphite connects the two electrodes in the furnaces. Two different types of SiC crystals may be obtained, i.e. green or black material. Green SiC is the purest material with >99% SiC, while the black material contains ~98% SiC. SiC may occur in a large variety of crystal modifications, i.e. polymorphs. In the Acheson process, the β-SiC is formed near the surface of the reacted material. This β-SiC modification is removed together with unreacted material, whereas the inner α-SiC is cleaned, crushed, and processed further. The raw product of pure SiC is processed in the refinery department, ending as a granular material with particle sizes in the range 0.2–200 μm.

During this production process, all the crystalline materials, i.e. quartz, cristobalite, graphite, and SiC fibres, are present in the work environment in addition to non-fibrous SiC dust. X-ray powder diffraction is the most suitable method to identify and quantify crystalline materials. For a direct determination of non-fibrous SiC with X-ray diffraction (XRD), we took a particular care for the selection of a diffraction line of SiC. This line should not interfere with the diffraction lines from other crystalline particulates in the work atmosphere.

A specific TLV value for respirable non-fibrous SiC dust of 3 mg m⁻³ has been set on the TLV list by American Conference of Industrial Hygienists (ACGIH, 2003). The application of X-ray powder diffraction makes it possible to determine the exposure to SiC dust for compliance work. Here, we report on a method for quantitative determination of non-fibrous SiC dust by X-ray powder diffractometry.

**MATERIALS AND METHODS**

**Material samples**

Material samples of non-fibrous SiC products from the three Norwegian SiC plants (i.e. A, B, and C) were used as standard materials. Pure SiC was used for the calibration of the quantitative method. Plant A produces green SiC and Plant B produces black SiC, whereas Plant C produces both green and black SiC. The standard materials chosen were products classified by the plants, according to the Federation of European Producers of Abrasives standard 42-1984 (revised 1993). The grain size is measured by photo sedimentation. Grain F1000 was selected to obtain a particle size close to the respirable fraction, the median particle size (D₅₀) being 4.5 μm (±0.8). These standard materials included two samples from different batches of each of the four SiC products obtained from the three plants. This gives four samples of green SiC (Plant A and C) and four samples of black SiC (Plant B and C).

**Sample preparation**

Separate calibration series were prepared for the four different SiC products, including materials from both batches. Three series each consisting of 10 filter samples were prepared with 0–1000 μg of SiC dust for all the four materials. A Sartorius MC 210 F microbalance, with a detection limit of 60 μg, was applied for gravimetric determination. All the samples were sonicated in a mixture of ethanol and water and deposited on polycarbonate filters with diameter = 25 mm and pore size = 0.8 μm, by wet filtration. The filters were dried at 60°C before the diffraction measurements. An α-ionizing unit was used to remove static electricity from the prepared filters (2U500-SM, Laborel corp.).

** Diffraction lines**

A typical X-ray diffractogram of the SiC calibration standard materials is shown in Fig. 1, with CuKα radiation (λ = 1.5418 Å). The present quantitative XRD method was developed for exposure assessment in the SiC industry. Thus, the 20 regions for the diffraction lines for quartz, cristobalite, and graphite had to be avoided (Altree-Williams et al., 1977; Bye, 1983). The primary peak of graphite (2θ = 26.66°) completely overlaps the primary peak of quartz. (Thus, the graphite has to be completely removed before quantitative determination of quartz in this industry.) Figure 1 shows diffractograms of all the four components, i.e. quartz, cristobalite, graphite, and SiC.

This combined XRD pattern is quite densely packed with diffraction lines. However, after a careful inspection of the 20 profiles, we selected the SiC reflections at 2θ = 35.59° and 71.70° as candidates for quantitative determination of SiC. These lines have no interferences with crystalline silica and graphite, minor interferences with cristobalite. Furthermore, the lines have strongly enough intensity for quantitative determinations for all practical purposes. Some of the major and the most relevant diffraction lines for the crystalline components are marked in Fig. 1. The concentration of crystalline SiC fibres in the working atmosphere is very low and we have neglected any interference from these particles. Analysis of the standard materials with scanning electron microscopy revealed no SiC fibres in the material samples (A. Skogstad, The National Institute of Occupational health, Norway). The scan ranges for the area integration of the two SiC diffraction lines...
are $2\theta = 34.80$–$36.40$ and $2\theta = 71.20$–$73.00$ for the two lines (002) and (112), respectively, with a scan speed of 0.01 degrees s$^{-1}$. The backgrounds were counted in 10 s at each end of the scan range.

**Diffractometry**

A fully automated Philip’s PW 1700 X-ray diffractometer was used for the analysis, equipped with sample spinner, graphite monochromator, proportional counter, a broad-focus CuK$\alpha$ X-ray tube ($\lambda = 1.5418$ Å), and a sample changer PW 1775. All the experiments were carried out with tube power at 50 kV and 50 mA, and the intensities were recorded at a rate of 0.01° 20 min$^{-1}$, with 1° divergence and receiving slits. The software package PC-APD (version 3.6) was used.

**Sample analysis and calibration**

All the calibration samples were analysed by X-ray diffractometry with a thin sample technique as described by NIOSH (1994), with some modifications described below. Absorption correction was obtained with the polycarbonate filter placed above a silver filter in the goniometer. The area of the diffraction lines was applied to determine integrated line intensities. Separate regression lines were constructed for all four material types presenting the area intensities as a function of sample weights. For practical use, all the regression lines were forced through origin.

**Quantitative calculations**

The thin sample model used in this study is a model proposed by PANalytical B.V. (1987, 2005). This model is suitable for mass calculation of small samples, such as air dust samples. The general formula is

$$M_i = I_{\text{conv}} \cdot B_{\text{im}} \cdot \ln(1/T),$$

where

- $M_i =$ calculated mass of compound $i$
- $I_{\text{conv}} =$ intensity of infinitely thick sample of compound $i$ (calculated and converted from the thin sample intensity)
- $B_{\text{im}} =$ mass calibration constant of compound $i$
- $T =$ transmission factor of the thin-layer sample

The mass is calculated after the measured intensity is converted as measured as a thick sample. Converted intensity ($I_{\text{conv}}$) is calculated according to

$$I_{\text{conv}} = I_i \cdot 1/(1 - T^S_i),$$

where

- $I_i =$ thin sample intensity of compound $i$
- $T^S_i =$ 1/sin$\theta_i$, where $\theta_i$ is the diffraction angle of compound $i$

The transmission factor ($T$) is calculated with the use of the intensity from a crystalline plate (for instance a silver membrane filter) before and after deposition of the dust:

$$T = (I_{\text{pa}}/I_{\text{pb}})^{\sin\theta_p},$$

where

- $I_{\text{pa}} =$ intensity of crystalline plate after dust deposition
- $I_{\text{pb}} =$ intensity of crystalline plate before deposition
- $\theta_p =$ diffraction angle of crystalline plate

**Fig. 1.** Diffractograms of quartz, cristobalite, graphite, silver, and SiC. Indices (hkl) of the specified diffraction lines: Q1 = 100; Q2 = 101; Q3 = 112; Q4 = 211; Q5 = 212/023/301; Cri1 = 101; Cri2 = 200; SiC1 = 002; SiC2 = 110; SiC3 = 102; C1 = 002; C2 = 101; Ag1 = 111; Ag2 = 200; Ag3 = 220.
All calculations were done with a quantitative software running on a personal computer developed by Lundgren and Lundström (2000). The intensity, diffraction angles, and other relevant data from all the measured peaks were automatically transferred to this special software. This software also corrects for any fall-off in the intensity from the tube by using an external monitor. Mass of the analyte \( m_{\text{analyte}} \) for each sample was calculated according to equation (4):

\[
m_{\text{analyte}} = K \times I_i + L,
\]

where \( K \) = linear calibration coefficient and \( L \) = intercept of the \( x \)-axis.

Values of \( 1/K \) and \( L \) were used for the quantitative determination of SiC in control samples, with mixtures of quartz and cristobalite. For practical use of the method, \( I/K \) and \( L \) are the key parameters for dust level determination.

**Quality control**

Participation in the interlaboratory proficiency analytical test (PAT) for quartz, described by Grunder (2003), accomplished the quality control of the diffractometric analysis. The quality control of the gravimetric procedures includes weighing of two standard filters before each weighing session. The Norwegian National Metrology Laboratory controls the balance.

**Statistical analysis**

Linear regression models were constructed and presented by SPSS 15.0 and Sigma Plot 2001.

**RESULTS**

Of the two chosen diffraction lines for the experiment, the final selected diffraction line for the quantitative determination of airborne non-fibrous respirable SiC dust is shown in Fig. 2. The intensity maximum is at \( 2\theta = 71.70^\circ \). We also tested the stronger diffraction line of SiC at \( 2\theta = 35.59^\circ \) for this method. However, this line showed anomalous interactions in dust mixtures with quartz and cristobalite, prepared with the standard materials for quality assurance of the method. This anomalous behaviour was difficult to explain and considered beyond the scope of the present investigation to explore.

Calibration samples of the four SiC materials, in the range 100–1000 \( \mu \)g, were accurately weighed and analysed by a sample XRD technique. Integrated intensities were used to relate intensity and sample weights. The diffraction peak was scanned in the range 71.20–73.00\(^\circ\) \( 2\theta \) and the backgrounds were counted for 10 s at each end of the scan range. These data were used for calibration and Fig. 3 shows all the various calibration data sets.

With a total of four different standard calibration data sets, the final calibration strategy could be four separate calibration sets, separate calibration sets for each of the three plants, or one calibration set with all the data pooled together. Table 1 shows relevant indicators for the validity of the calibration sets. Although the correlation coefficient \( (R^2) \) is somewhat lower for the pooled set, this set was selected for practical reasons. One calibration set is obviously easier to handle than three or four different sets. The regression model through origin was.

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**Fig. 2.** A close up diagram of the selected SiC peak, together with the corresponding diffraction diagrams for quartz and cristobalite. See Fig. 1 for indices of the diffraction lines. Indices \((hkl)\) of the specified diffraction lines: \(Q6 = 104; Cr3 = 105; Cr4 = 313; Cr5 = 322; SiC3 = 102.\)**
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Fig. 3. The calibration curve used for quantitative determination of non-fibrous SiC. This data set includes all the four material types, i.e. A-G, B-B, C-G, and C-B. $R^2 = 0.98$.

Table 1. Statistical parameters for the selection of calibration model, for the quantitative determination of non-fibrous SiC dust

<table>
<thead>
<tr>
<th>Material type</th>
<th>Standard error for $a^a$ (µg SiC per count)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-G</td>
<td>0.006</td>
<td>0.31</td>
</tr>
<tr>
<td>B-B</td>
<td>0.008</td>
<td>0.26</td>
</tr>
<tr>
<td>C-G</td>
<td>0.007</td>
<td>0.29</td>
</tr>
<tr>
<td>C-B</td>
<td>0.006</td>
<td>0.25</td>
</tr>
<tr>
<td>All four</td>
<td>0.005</td>
<td>0.28</td>
</tr>
</tbody>
</table>

Forced through origin

<table>
<thead>
<tr>
<th>Material type</th>
<th>Standard error for $a^a$ (µg SiC per count)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-G</td>
<td>0.003</td>
<td>0.30</td>
</tr>
<tr>
<td>B-B</td>
<td>0.005</td>
<td>0.24</td>
</tr>
<tr>
<td>C-G</td>
<td>0.004</td>
<td>0.28</td>
</tr>
<tr>
<td>C-B</td>
<td>0.003</td>
<td>0.24</td>
</tr>
<tr>
<td>All four</td>
<td>0.003</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Four separate calibration data sets, A-G, B-B, C-G, and C-B, in addition to the pooled set were evaluated. Each separate calibration set includes 30 samples, except for C-G, with only 29. One sample was damaged and had to be discarded.

$^a$The calibration line is calculated by the equation $Y=\alpha x + b$, i.e. $m_{\text{analyte}}=K \times I + L$, see equation (4).

selected. The calculated values of $K = 1$/calibration constant and $L = 0$ [see equation (4)] were introduced in the regression line for calculation purposes.

The limit of detection (LOD, instrumental) was determined to be 12 µg, based on the lowest observable value above the background intensity level in the 2θ region of the selected SiC diffraction line. The limit was set to three times the standard deviation of the background intensity.

DISCUSSION

The main objective for the present work was to develop a method for quantitative determination of respirable non-fibrous SiC dust. This method should first of all be applicable for the industrial production of SiC, for assessment of dust exposure. The present method has a level of detection of 12-µg non-fibrous SiC dust. The selection of a stronger X-ray reflection would have improved the LOD. However, our choice had to consider the many possible interactions by quartz, cristobalite, and graphite.

Mattenklott (2005) has described a similar method for the determination of SiC dust in the Laboratory Workbook of Berufsgenossenschaftliches Institut für Arbeitsschutz (BGIA). He uses three diffraction lines for the determination, including the line at $2\theta = 61.00^\circ$, see Fig. 1. In the description, it is stated that quartz and cristobalite may be determined on the same filter as SiC. This works perfectly for the line selected in our method, the line at $2\theta = 71.70^\circ$. However, the line at $2\theta = 35.59^\circ$ has not been encountered, being evident only for mixed materials with quartz, cristobalite, and SiC. One point of minor importance is the slightly larger LOD for the BGIA method, although the levels are of the same order of magnitude. For personal samples, with a restriction of only 2 h dust collection (in the case of the BGIA method), a LOD of 40 µg as compared to our LOD of 12 µg is reported.

No international standard material exists for non-fibrous SiC. Thus, pure SiC products from the three Norwegian plants were used as calibration materials. We have applied this method in a comprehensive exposure assessment in the Norwegian SiC industry reported by Føreland et al. (2008). The exposure level of SiC dust in this investigation was found to be in the range 12–890 µg m$^{-3}$. Further details may be found in the original article. All these results will be used to refine the JEM of Romundstad et al. (2001). Next, the refined JEM will be used in epidemiological studies. The main question is ‘Are there any causal associations between the airborne risk factors and lung cancer and other lung diseases in the SiC industry?’

Recently, ACGIH (2003) suggested a TLV of 3 mg m$^{-3}$ for respirable non-fibrous SiC dust. Thus, an LOD of 12 µg is fully acceptable and applicable for compliance work. The present method is operating along the same principles as other well-established and internationally evaluated X-ray powder diffraction methods (NIOSH, 1994). In practice, dust samples in the range 1–2 mg may be analysed as a result of an 8-h sampling time. This corresponds to a respirable dust level of 1–2 mg m$^{-3}$. However, in the furnace hall of this specific industry, the airborne dust levels should be much lower. This is due to the presence of the carcinogens quartz and cristobalite. Hence, it is important that the LOD of an analytical method is comparable with safe exposure levels, taking into considerations all the airborne chemical hazards.
The work atmosphere in the SiC industry is very complex. According to European Standard EN689, a suggested safe and acceptable exposure level is less than one-fourth of the actual TLV (European Standard, 1995). In the SiC industry, the crystalline component cristobalite is a risk factor with a quite low TLV for respirable dust, i.e. 50 μg m⁻³. An acceptable LOD for the quantitative determination of cristobalite should thus be ~12 μg. Quantitative determination of cristobalite by X-ray diffractometry has an LOD of 5–10 μg, fully accomplishing the criteria of detection limit.

A corresponding evaluation of the present method shows a ratio for LOD/OEL (i.e. occupational exposure level) or LOD/TLV of ~1/300 for SiC dust. Thus, for the quantitative determination of non-fibrous SiC respirable dust, the presented method is fully applicable.

Although the described method is fully applicable for compliance work, some improvements is still possible for the determination of airborne SiC dust:

- an international standard material with adequate particle-size distribution, i.e. respirable or inhalable fraction, would highly simplify and improve the quantification of SiC dust exposure.
- if the X-ray method is to be used in work environments with no interferences from other crystalline components, a diffraction peak with higher intensity than 20 = 71.70° could be selected for the determination of SiC.

However, exposure assessment of SiC during the industrial production of this material has to consider the interferences from quartz, cristobalite, and graphite. Small differences in the crystallinity of SiC produced at different SiC plants may give rise to a need for intra-plant standard materials. In such cases, international specifications of material purity and properties should be given, to obtain the most precise exposure level to non-fibrous SiC dust.

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