

# The Measurement of the Exposure of Workers to Respirable Crystalline Silica (RCS) and the Work of the International Standard Organisation (ISO) Working Group TC146/SC2/WG7 Silica

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**ABSTRACT:** This paper reviews the issues associated with the measurement of RCS and the work of the ISO working group in this field. Silica is one of the most abundant minerals on earth and silicosis is one of the world's oldest known occupational diseases caused by the inhalation of RCS, which is classified as a category 1 carcinogen by the International Agency for Research on Cancer. Various work processes can create large amounts of respirable dust that can be controlled by wet suppression and/or ventilation. However, levels of RCS above those that are considered acceptable can still persist in the workplace. Measurement of RCS is increasingly challenging because the pressure for lower exposure limits reduces the mass of analyte that is collected and increases the relative error and uncertainty.

Many countries propose a limit of  $0.05 \text{ mg.m}^{-3}$  for an 8-hour sample. As many work activities are sampled for 4-hours or less, some measurements are likely to be close to the limits of quantification of the measurement instruments currently used, and may not meet accuracy requirements for occupational hygiene measurements, such as EN482 in Europe. This may have implications if the differences between results are disputed.

Agreement of measurements between laboratories will be difficult to achieve at this level without a collaborative approach to standardise procedures and control and monitor their quality. The ISO working group is developing a strategy to improve the reliability of these measurements by providing guidance to both the analysts and the individuals commissioning work. The first guidance document discusses key areas of RCS measurement that can affect the accuracy, such as sampling equipment, the analytical approach, the standards used and specific instrumental tests that need to be followed.

**Key words:** - silica, respirable crystalline silica, measurement, quality, guidance.

## 1 INTRODUCTION

### 1.1 Silica

Silica is one of the most abundant minerals on earth and it exists in a number of crystalline and amorphous forms; the most common of which is quartz. This is found in a range of sandstones, grit stones, clays and shales. The quartz content of sandstone may be near 100 % and granite stone may be as high as 30 %. Many industrial activities, such as drilling, chiselling, grinding and power saw cutting of stone, concrete, or brick, polishing of glass, fettling in potteries and demolition of buildings, result in the generation of respirable crystalline silica (RCS).

### 1.2 Silicosis

Silicosis is one of the world's oldest known occupational diseases and is caused by the inhalation of respirable crystalline silica, which is classified as a category 1 carcinogen by the International Agency for Research on Cancer (IARC 1997). Silicosis is a progressive, irreversible disease that often takes years to develop. It hinders the efficiency of breathing and can be severely disabling. Silicosis impedes the quality of life for many workers and, in severe cases, leads to premature death. Heavy and prolonged exposures to RCS under conditions that produce silicosis can also cause lung cancer.

### 1.3 Exposure

In all countries, large groups of workers are potentially exposed to RCS, because of abundance of free silica and the range of industrial tasks involving materials containing free silica. In many countries the improvements in workplace control standards has reduced the scale of the reported cases of silicosis. Some countries have also banned silica from its use as a blasting material because this task using sand was identified as a major cause of silicosis cases. However, even where national legislation has for many years required the employer to implement control standards there remains a persistent level of reported silicosis cases. This failure to eliminate or reduce the incidence of silicosis at the current occupational exposure standards has increased the pressure for a reduction in the exposure limits and for tighter controls (Wagner 1995).

## 2 OCCUPATIONAL EXPOSURE STANDARDS

### 2.1 Risk of Silicosis

Evidence suggests the risk of developing silicosis is dependant of the nature and physical treatment of the material during a work activity. For example, RCS generated by fracturing the surface of a material is often considered more hazardous than geologically 'aged' RCS (Vallyathan 1995) and the use of machine tools can generate very high levels of respirable dust that contain RCS. There are many epidemiological studies that show a health risk below the current occupational standards (National Institute for Occupational Safety and Health, 2002). A recent health risk review document published by the Health and Safety Executive (HSE) in the United Kingdom (HSE 2002) describes the relationship of the risk of developing silicosis, within 15 years, after 15 years of exposure.

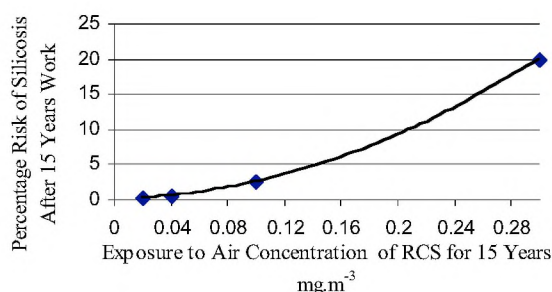


Figure 1: Risk of developing silicosis from machine generated RCS.

The majority of data used in the hazard evaluation are from coalminers using machine tools to cut through sandstone, as this was considered as the most reliable study available. A level where the risk of silicosis is completely eliminated was not identified from the HSE study. However, data suggest that the risk of developing silicosis is about 0.5 % (1 person in 200) at an RCS in air concentration of 0.04 mg.m<sup>-3</sup> and 2.5 % at 0.1 mg.m<sup>-3</sup>.

### 2.2 Current exposure Standards

A selection of current occupational exposure standards for RCS is shown in Table 1.

Table 1: A selection of occupational exposure standards for RCS (mg.m<sup>-3</sup>)

| Country        | Quartz           | Cristobalite     | Tridymite        |
|----------------|------------------|------------------|------------------|
| United Kingdom | 0.3 <sup>#</sup> | 0.3 <sup>#</sup> | 0.3 <sup>#</sup> |
| Finland        | 0.2              | 0.1              | 0.1              |
| South Africa   | 0.2              | 0.2              | 0.2              |
| Austria        | 0.15             | 0.15             | 0.15             |
| Germany        | 0.15             | 0.15             | 0.15             |
| France         | 0.1              | 0.05             | 0.05             |
| Netherlands    | 0.075            | 0.075            | 0.075            |
| Italy          | 0.05             | 0.05             | 0.05             |
| Ireland        | 0.05             | 0.05             | 0.05             |

<sup>#</sup>The occupational exposure standard is currently under review and it is expected the United Kingdom will change the standard to 0.1 mg.m<sup>-3</sup> in 2006.

These standards range from 0.3 to 0.05 mg.m<sup>-3</sup>.

The European scientific committee for occupational exposure limits (SCOEL) has recommended that to eliminate silicosis occupational exposure standards should be set below 0.05 mg.m<sup>-3</sup>. It is possible that the exposure standards listed in Table 1 are not all comparable, as they do not have the same legal status in each country (Walters et al 1995).

## 3 MEASUREMENT

Measurements are needed to ensure compliance with regulations to protect the health of the worker and to monitor the effectiveness of control methods. It is important that exposure measurements are reliable, since measurement levels with low accuracy may lead to discrepancies in interpretation and mislead the occupational health professional. Good accuracy increases the confidence in data and helps identify when peak exposures are not effectively controlled. Some work activities that expose people to RCS involve work outside a factory environment, in the open air or in confined spaces, and it is not easy to introduce some types of controls to reduce the incidence of high peak exposures.

### 3.1 Analytical Techniques

The most common approach to monitor respirable dust is gravimetric analysis. However, weighing is not analyte specific for RCS, although it is a useful screening technique for samples requiring further analysis. The most commonly described techniques in methods used for the analysis of RCS are x-ray diffraction and infrared analysis (Madsen, 1995) although microscopy methods (counting of quartz particles) and colorimetric techniques are also still used in some countries.

#### 3.1.1 Infrared Technique

This instrument detects silica from the absorbance of infrared by the silicon and oxygen bonds at 780 and 800  $\text{cm}^{-1}$  for quartz and 620 and 800  $\text{cm}^{-1}$  for cristobalite. The silica is quantified using the Lambert-Beer law, however, other silicates and non-crystalline silica with similar Si=O vibrational stretches will interfere with quantification. This technique has routinely been used for samples from coalmines where the crystalline carbon (graphite) causes an interference problem for the most sensitive quartz reflection for x-ray diffraction. Mathematical routines are available that estimate the amount of interference from the intensity of absorbances that are distinctive of the interfering component, such as kaolinite, and calculate a correction (Mine Safety and Health Administration 1994). An infrared instrument is less expensive to purchase than an x-ray diffraction instrument and is more commonly used in small commercial laboratories.

#### 3.1.2 X-ray diffraction

This is a reflectance technique where a crystalline component of a powder will reflect a distinctive pattern when placed in a beam of focused x-rays. The distinctive pattern of reflections is specific to the crystal structure. The technique is less susceptible to problems with interfering components than the infrared technique. This is because another reflection can be selected for quantification if the most sensitive reflection within the pattern is subject to interference from other crystalline components.

## 4 ANALYSIS METHODS

There are two distinct analytical approaches used in methods for RCS. These are:

- The direct on-filter (DOF) analysis approach where the dust in the air is collected using a particle size selector onto an air filter that is then presented to the instrument for analysis.
- The indirect analysis approach where the dust from the air filter is recovered and re-deposited on or in another substrate and then analysed.

The choice of approach is often dependant on the type of sampler used to collect the respirable fraction. Samplers are predominantly designed to collect the dust on a filter for gravimetric analysis and the requirements for further analysis using infrared or x-ray diffraction are not a primary consideration. The DOF approach requires a size of filter of about 25 mm, where the majority of the sample is examined in the x-ray or infrared beam; so size selector devices that require larger diameter filters or use foam pads are not suitable.

Both analytical approaches and instrumental techniques have similar limits of detection and quantification when interferences are absent. However, when interferences are present the analytical sensitivity is reduced. In x-ray diffraction a less sensitive reflection is often chosen that increases the limit of detection. The indirect analysis approach may allow scope for the treatment of the sample to remove the interferences. However, this additional process also increases the possibility of sample losses and low recoveries and is not always effective. The additional analytical processes also significantly increase the cost of analysis.

## 5 ANALYTICAL PRECISION AT THE PROPOSED EXPOSURE LIMITS

Increasingly, international organisations are establishing criteria for the analytical performance of methods, when measuring occupational hygiene samples at the exposure limits. In Europe, the standard EN482 (British Standards Institute, 1994) requires the uncertainty of a measurement, including sampling, to be within  $\pm 30\%$  at the exposure limit and  $\pm 50\%$  at about half the limit value. In the United States the National Institute of Occupational Safety and Health (NIOSH) stipulates an accuracy requirement, including sampling, of  $\pm 25\%$ . Figure 2 shows the relationship between the percentage relative standard deviation and measurement level between laboratories using direct on-filter analysis methods in the proficiency-testing programme the Workplace Analysis Scheme for Proficiency (WASP) (Stacey, 2003). This shows that between the analytical range 80 – 400  $\mu\text{g}$  the average relative

standard deviation gradually increases from about  $\pm 6\%$  at  $317\text{ }\mu\text{g}$  (the mass on the filter sampled for 8 hours at  $2.2\text{ l.min}^{-1}$  from an RCS in air concentration of  $0.3\text{ mg.m}^{-3}$ ) to about  $9.6\%$  with  $106\text{ }\mu\text{g}$  on the filter (the mass on the filter sampled for 8 hours at  $2.2\text{ l.min}^{-1}$  from an air concentration of  $0.1\text{ mg.m}^{-3}$ )

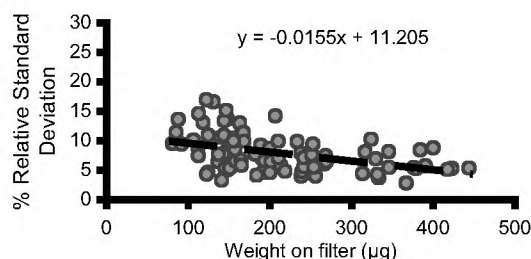


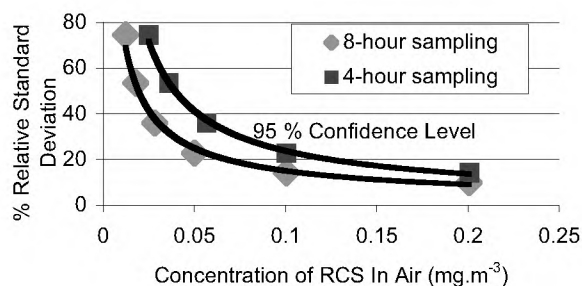
Figure 2: The relationship between relative standard deviation (RSD) and weight measured for on-filter analysis methods.

Generally, when the analytical technique approaches its limit of quantification, the relative standard deviation of measurements, increases as the mass measured decreases. The relationship in Figure 2 together with Table 2 shows that the measurements, at the masses measured in the WASP programme, are just above the limit of detection. If the occupational exposure limits are lowered below  $0.1\text{ mg.m}^{-3}$  then the mass that is measured is also reduced below the range shown in Figure 2. Table 2 shows the masses of dust that are collected on the filters with cyclone samples operating at a flowrate of  $2.2\text{ l.min}^{-1}$  for various RCS in air concentrations. The levels chosen represent established or proposed occupational exposure limits for RCS.

Table 2: Mass ( $\mu\text{g}$ ) measured on the filter at various air concentrations

| Air Concentration<br>$\text{mg.m}^{-3}$ | Mass Measured<br>Sampling Period |         |
|-----------------------------------------|----------------------------------|---------|
|                                         | 8 hours                          | 4 Hours |
| 0.2                                     | 211                              | 106     |
| 0.1                                     | 106                              | 53      |
| 0.05                                    | 53                               | 26      |
| 0.025                                   | 26                               | 13      |

Measuring a smaller mass will also increase the relative precision. Figure 3 shows the predicted relationship between the average RSD of measurements between laboratories for the masses listed in Table 2



for direct on-filter methods when measuring a filter with HSE silica standard A9950.

Figure 3: Predicted distribution of results between laboratories

Figure 3 shows that at an RCS in air concentration of  $0.05\text{ mg.m}^{-3}$  some measurements on a sample of 4 hours duration from laboratories are unlikely to achieve the uncertainty requirements of EN482. At the masses measured for RCS air concentrations below  $0.05\text{ mg.m}^{-3}$  the relative error increases with relatively small decreases in air concentration, which suggest that the measurements are approaching the limits of the analytical method with the current instrumentation (Smith 1997). Individual laboratories may achieve better precision than is suggested by the values in Figure 3, especially, when the most sensitive peaks measured using x-ray diffraction are free from interference. However, the additional complications with interferences will also increase the uncertainty of results. Analysts can remove interferences by adopting the indirect analysis approach and by chemically treating the air filter before the instrumental measurement but without proper controls this approach can achieve low recoveries from losses during the process removing the filter and re-deposition (Miles 1999). Digestion of some interfering minerals with phosphoric acid may also produce amorphous silica that will affect infrared analysis unless this is completely removed. These digestion processes require the use of powerful and hazardous acids. Recent work (Kauffer 2005) also show that differences between the analytical approaches measuring the same sample in the same laboratory differ more significantly below  $0.05\text{ mg.m}^{-3}$ . Therefore, the current evidence suggests that measurements of silica in air concentrations of  $0.05\text{ mg.m}^{-3}$  measured by different laboratories will differ significantly; especially when the samples contain interferences and different analytical approaches are used. These differences may lead to disputes between laboratories when legal cases are pursued.

## 6 MEETING THE CHALLENGE

The challenge is for laboratories to help industry to demonstrate that their control systems and methods of work comply with national occupational control standards by reliably measuring the mass of silica on a filter from short duration samples (less than 4 hours) from a workplace atmosphere containing  $0.05\text{ mg.m}^{-3}$ . If the occupational standard for RCS is  $0.05\text{ mg.m}^{-3}$  and the air was sampled for only 4 hours (a volume of 528 litres) the challenge is demonstrate a

laboratory can sample and reliably measure 26 µg of quartz or cristobalite on a filter. The challenge is more difficult for shorter duration samples since the limit of detection (LOD) for many analysis methods for silica is between 6 and 10 µg and the 95 % confidence intervals of measurements at the present LODs are likely to coincide with the 95 % confidence intervals of the analytical measurements of masses below 26 µg with the methods currently employed.

This challenge is being tackled in several ways.

- 1 Developing size selectors and sampling procedures to obtain larger volume samples
- 2 Using improved instrumentation in x-ray diffraction.
- 3 Providing internationally agreed guidance to help control the errors in measurement
- 4 To require laboratories to demonstrate quality such as participation in a proficiency testing programme and/or accreditation

## 6.1 Larger volume samplers

### 6.1.1 Cyclones

A cyclone is designed so that its physical dimensions at a specific flow rate select a given size range of dust particles from the ambient air. Therefore, the sample volume sampled by the filter is limited by the design of the cyclone. Most cyclone type respirable samplers require a flow of air of between 1.7 – 2.2 l.min<sup>-1</sup>. The GK 2.69 (BGI Inc, USA) has a rate of 4.2 l.min<sup>-1</sup> that allows twice the usual sampling volume to be taken. This GK 2.69 cyclone is only available for 37 mm filters at the moment. Work to adapt and characterise the performance with this type of cyclone for 25 mm filters is under consideration at the Health and Safety Laboratory in the United Kingdom.

### 6.1.2 Foam Pad Samplers

Samplers that use foam collection substrates such as the CIP 10 sampler can use much higher flow rates (10 l.min<sup>-1</sup>). However, this sampler is likely to collect significantly more dust than a filter and an indirect analysis approach is needed to recover the dust from the foam. If the sample is very dense it will be opaque to the infrared beam and this technique may have problems analysing some heavily loaded samples. X-ray diffraction analysis may be able to analyse heavily loaded samples, but this technique will

have to take into consideration additional matrix and sample absorption effects.

## 6.2 Improved instrumentation

An array detector used with x-ray diffraction instruments can collect 10 times more counts during the same amount of time than existing instrumentation with traditional proportional or scintillation detectors. As array types of detectors for x-ray diffraction become increasingly common, the counting precision and sensitivity at low mass measurement levels should improve.

## 6.3 ISO Working Group

The international pressure in lowering the occupational exposure limits has increased the urgency of some national organisations involved in the measurement to share experiences and work together to ensure measurements are comparable. The initial approach agreed at an International Standards Organisation (ISO) working group ISO/TC146/SC2/WG7 silica is to provide two levels of guidance that are targeted at analysts, to ensure the quality of the measurements, and the occupational health professional commissioning and interpreting the exposure monitoring.

### 6.3.1 Guide for ensuring the quality of measurement

Work at the American National Institute for Occupational Safety and Health (NIOSH) evaluating results from the American Industrial Hygiene Association (AIHA) proficiency analytical testing programme (PAT) identified several factors that may improve the consistency (Eller 1999). Some of these factors are being incorporated into a draft document titled, 'Ensuring the quality of respirable crystalline silica measurements'. The approach used in this proposed guidance is to take into consideration all the factors that may influence a measurement using a cause and effect diagram. This is similar to the approach used in the ISO Guide for Uncertainty Measurement document (ISO 1995), when identifying the factors that may contribute to the overall uncertainty of a measurement. An example is shown in Figure 4

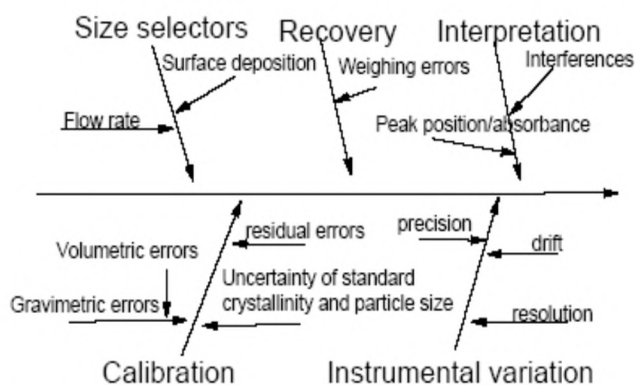


Figure 4: A cause and effect diagram for the uncertainty of silica measurements

The document will then provide guidance about how to control each of these variable factors. Examples include:

- Comparing the crystalline content and particle size distribution of the calibration standard against a certified material
- Encouraging the measurement of a significant number of calibration standards
- Applying recovery and quality control checks and correcting for differences with the expected result
- Applying instrumental checks for drift, peak position and resolution
- Interpretation

### 6.3.2 Silica dust calibration standards

The instrumental response of both the infrared and x-ray diffraction instruments are influenced by the particle size distribution of the analysed material. In x-ray diffraction, the peak height increases with increased particle size and for infrared the response decreases with increase particle size. There are several different dust standards available in different countries, each containing a slightly different particle size distribution and crystalline content. There are two issues with the dust standard that need addressing:

1. Some laboratories may assume that their calibration standard is all crystalline and not correct for the amorphous content that is associated with this material.
2. The calibration procedures applied with the different analytical approaches may subtly alter the particle size distribution of the original standard.

Laboratories should apply a correction factor to account for the particle size distribution and crystalline content effects.

### 6.3.3 Calibration Standards

Results from the PAT program (Eller 1999) showed that some laboratories were using as few as 3 standards to calibrate their instruments. Work has shown that for the most sensitive peaks for x-ray diffraction particle statistics and the subtle differences in the way the dust is distributed on the filters make a far larger contribution to relative error than counting statistics (Chisholm 1994). If the number of calibration standards is increased the contribution of standard error of the calibration line to the overall error in analysis is reduced. To improve the statistics at lower measurement levels it is important to measure as many calibration standards as possible or make repeat measurements on the standards that are available. The guidance will recommend 3 repeat measurements on 6 concentration levels if using the indirect analysis approach or the analysis of a minimum of 20 calibration filters covering the likely range of concentration levels.

### 6.3.4 Recovery Checks

The indirect analysis approach includes a process where dust is recovered from the filter and is deposited onto another substrate such as a silver filter. This process can introduce additional errors and a negative bias if sample is lost (Miles 1999). To control this, laboratories should include quality control evaluation or check samples in the analysis process and correct for any consistent low recovery. These check samples can either be prepared from a calibration suspension or purchased from a proficiency-testing provider.

### 6.3.5 Instrumental Variation

#### 6.3.5.1 Energy Drift (Response)

For optimum X-ray diffraction instrument performance, the X-ray source must be aligned and monitored routinely for stability. An estimate of instrumental drift should be performed on a routine basis. The intensity of the x-ray radiation from the source deteriorates over time and a correction should be applied to correct for the instrumental drift. An aluminium plate or any other suitable stable robust material can be used as an external standard to correct for the gradual decline in X-ray tube emission. Such a standard should be fine-grained, free from marked texture and have a strong X-ray diffraction peak in roughly the same position as the quartz or cristobalite peaks being used for analysis. Modern infrared instruments are less subject to drift; however, the laser intensity (energy) should be checked periodi-

cally as this will also provide a check to determine if the analysis conditions have been altered.

#### 6.3.5.2 Resolution

Most modern infrared instruments employ their own internal checks for wavelength drift and the absorbance of silica is a relatively broad peak. However, the ISO standard will recommend that the resolution should be set at about 8 wave numbers ( $\text{cm}^{-1}$ ). In x-ray diffraction it is more necessary to check the resolution routinely with a standard reference material such as NIST 640c or other well characterised material since this is a reflectance technique and the sample height or detector movement may change.

#### 6.3.6 Interpretation

One of the critical aspects of the silica analysis is the interpretation of the spectra. It is important that the individual interpreting the results is provided with information about the environment in which the sample was taken, since they will need to assess the affect of any interference present. At very low levels, the reported value is dependant on the approach used to interpret the spectra. In x-ray diffraction, subtle changes in sample height can cause a peak shift that may need accurate interpretation.

#### 6.4 Demonstration of quality

From a regulatory view it is important that the quality of measurements is sufficiently accurate so that results between laboratories are comparable. If measurement levels are reduced to  $0.05 \text{ mg.m}^{-3}$  then it is likely that disagreements of the reported measurement value between laboratories will be more frequent. In similar circumstances, where the potential variability of results between laboratories is large, such as for asbestos exposure analysis, many countries require the accreditation of laboratories and their participation in proficiency testing programs. Although accreditation and the participation in proficiency testing is recognised as good practice, few countries require this for laboratories analysing silica. This may change, particularly the requirement for laboratories to participate in proficiency testing, since participation in this is one of the few ways a laboratory can assess the potential bias of its measurements and investigate any differences that occur.

## 7 CONCLUSION

With the current instrumentation and methods used for the measurement of RCS it will be difficult to demonstrate compliance or regulate with measurement, if an occupational exposure standard is established as  $0.05 \text{ mg.m}^{-3}$  or less. The challenge is to develop procedures and techniques to improve the measurement before exposure standards are reduced to this level. A multi-faceted and multi-disciplined national and international approach is being developed to overcome this challenge. This includes development of existing technologies to improve precision and the amount of mass measured on the filter, international collaboration to provide guidance to control the errors in measurements and some national measures to improve and maintain satisfactory analytical performance.

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