

Infrared Spectroscopy

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At-Site Direct-on-Filter End-of-Shift Portable FT-IR and Fast Respirable Crystalline Silica Quantification

Scope

This application note describes a non-destructive analytical method to quantify respirable crystalline silica (RCS) deposited on sampling filters, at the end of a shift (EoS), at site where sample collection has occurred. Respirable dust, sampled from the breathing zone

of the worker, is deposited onto a polyvinyl chloride (PVC) filter to provide an estimate of the employee's exposure to airborne contaminants. Infrared spectra are collected in transmission mode through the PVC filter and are analyzed for crystalline silica content. Field Analysis of Silica Tool (FAST) software, developed by the United States National Institute for Occupational Safety and Health (NIOSH), is used to store all relevant details in a single location regarding the analysis including worker location and task for easy exposure monitoring.

Introduction

Silicon is the second most abundant element in the earth's crust and comprises approximately 27% of the average rock.^[1] Crystalline silica, a class 1 human carcinogen^[2], is a common constituent of rocks, soil, and sand. Crushing, drilling, grinding, masonry, concrete work, sandblasting, and mining of silica containing rocks, soil, and sand results in the generation of respirable crystalline silica (RCS) dust. Respirable dust corresponds to the fraction of inhaled dust and dust particles which penetrates to the gas exchange region of the lungs^[3]. Several studies indicate the correlation between occupational exposure to RCS dust and health effects including silicosis, lung cancer, pulmonary tuberculosis, and chronic obstructive pulmonary disease^[4]. Auto-immune diseases such as scleroderma, rheumatoid arthritis, and system lupus erythematosus have all been associated with exposure to RCS dust^[5]. Silicosis is an irreversible

chronic fibrotic lung disease, and this leads to scarring of the lung tissue, a decreased lung function, and respiratory failure this is, however, associated with the inhalation of RCS dust [6 & 7]. Silicosis is preventable through exposure control and timely implementation thereof [8]. To effectively control exposure to RCS, employers need to ensure that air- and health monitoring, is conducted routinely through sustainable methods. Legislative requirements pertaining to occupation exposure limits and monitoring of silica emphasize the importance of exposure control [9].

Exposure control for RCS begins with sampling the breathing zone of workers throughout their workday [10 & 11]. This is accomplished using various personal dust monitors which utilize a pump to pass air from the breathing zone through a PVC filter. The PVC filter collects the dust contained within the sampled air for subsequent analysis. Several examples of sampling cassettes which house the PVC filters are shown in Figure 1. The PVC filters are collected and submitted for analysis after sampling at least 80% of the worker's shift. Should analyses indicate that RCS in sample filters exceed the safe levels, an overexposure investigation must be conducted.

Workplaces are dynamic, especially in the mining industry. Work sites are constantly moving into new and often different geological strata having varying levels of silica. Traditional analysis methods currently employed may present a time lag of weeks before exposure data is received. As such the information is often of little use to inform decision makers of workplace conditions aimed at preventing overexposures. Traditional methods of RCS filter analysis can be expensive and labor intensive. Turnaround times for results can range from a few days up to several weeks depending on location and analysis method. The turnaround time is constrained by the distance between the sampling site and the laboratory, transport arrangements to the site, as well as the workload of the specific laboratory. Mining sites located in remote areas often need to send samples to a significantly distanced geographic location or even a different country due to the unavailability of appropriate laboratory facilities.

FT-IR KBr Pellet

Traditionally, filter analysis is either conducted using Fourier Transform Infrared Spectroscopy (FT-IR) or X-ray diffraction (XRD) techniques. Several published methods, NIOSH Method 7602 and MDHS101/2 have been developed by regulatory bodies for analysis of RCS [12 & 13]. NIOSH Method 7602 is a destructive technique which involves ashing of the PVC filter and pressing to form a potassium bromide (KBr) pellet out of the remaining material. Sample quantity has an influence on the clarity of the pellet, when the ashed sample filter is added to the halide salt (KBr). It is essential that the sample

is thoroughly blended with the KBr powder to ensure that the KBr pellet that is produced enables an accurate spectra acquisition. The overall quality of a pellet is mainly dependent upon the quality of the KBr powder used, which should always be of analytical grade purity. The pellets are analyzed using FT-IR and quantitation is performed through the development of a calibration curve with prepared standard reference materials.

X-Ray Diffraction (XRD)

XRD permits direct on filter analysis of respirable dust samples where the filter is placed within the beam path of the instrument. XRD peaks are produced by constructive interference of a monochromatic X-ray beam which scatters at specific angles from each set of lattice planes in a sample. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the XRD pattern is the fingerprint of the atomic arrangements in each material. Standard reference materials (SRM) are used to create the calibration curve, for the determination of RCS content. The DoF XRD method consists of placing a filter inside sample holders inside the X-ray diffractometer. Dependent on the type and model of instrument used, a mechanism picks up the samples one-by-one to be analyzed.

FT-IR Direct on Filter (DoF)

The DoF FT-IR method outlined in MDHS101/2 was developed specifically for the quantification of RCS on samples obtained using a Higgins-Dewell design type cyclone and is only suitable for the analysis of 25 mm diameter or smaller filters [14]. This method is not suitable for analysis of short-term exposure measurement samples (15 minutes).

FT-IR At-Site EoS DoF

The proposed At-Site EoS DoF FT-IR FAST method differs from the MDHS101/2 DoF FT-IR method in terms of the capabilities offered [15]. The FT-IR analysis is carried out using a PerkinElmer Spectrum Two™ FT-IR spectrometer (Figure 2). The At-Site EoS DoF FT-IR method is suitable for a variety of filter sizes, sampling durations and sample types. Additionally, the FAST software provides the user with easily interpretable results in an organized database.



Figure 1: Representation of a standard 3-piece sampling cassettes from Sedulitas (A). Representation of the 4-piece "shoot through" sampling cassettes (B).



Figure 2: PerkinElmer Spectrum Two™ FT-IR Spectrometer.

The At-Site EoS DoF FT-IR analytical method sequence diagram (Figure 3) is the simplified explanation of how this method works. When an RCS exposure hazard is identified within a work environment, the level of exposure is measured by taking a personal exposure sample with a constant velocity flow pump. The sample can be analyzed using the At-Site EoS DoF FT-IR method on site at the end of the shift or the following day. The results can be evaluated to determine whether the exposure values measured are within acceptable levels as stated by the relevant legislation. If the At-Site EoS DoF FT-IR method indicates an overexposure, the incident can be investigated immediately.

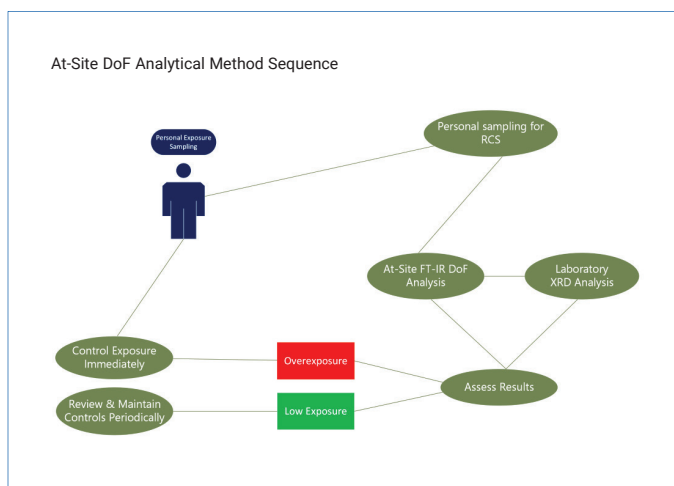


Figure 3: Flow diagram indicating the At-site DoF method process.

The method is also suitable to use for periodical review of control measures. A sample can be taken in an area and analyzed with the At-Site EoS DoF FT-IR method and results can indicate whether current control measures are efficient to eliminate or reduce RCS exposure. The At-Site EoS DoF FT-IR analytical method has been specifically designed for respirable alpha quartz, which is the most common crystalline silica polymorph.

Experimental

Sample Preparation

Sampling media were prepared by weighing a clean, unused PVC filter on an analytical microbalance in accordance with general methods for sampling and gravimetric analysis of respirable, thoracic, and inhalable aerosols (method MDHS14/4 issued by the Health and Safety Laboratory of the Health and Safety Executive (HSE), UK). Weighed filters were then secured by placing them in designated sampling cassettes. The exterior of the cassettes was marked to indicate the initial weight and size of the filter and placed inside. For this data collection experiment, 37 mm diameter PVC filters were used in conjunction with a 4-piece sampling cassette, a cyclone, and a personal sampling pump set to an average flow rate of 2.2 L/min. On the day of data collection, a prepared sampling cassette was attached to a cyclone and connected to a personal sampling pump.

The sampling apparatus was worn by workers for a duration of at least 7 hours or approximately 80 % of the worker's shift. At the end of the data collection period the sampling cassettes were removed and details regarding the type of work and workers' location on-site was recorded. Figure 4 shows examples of PVC filters following a data collection event. Data collection was conducted on a total of 17 days, spanning over a 2-month period, at an opencast iron ore mine located in South Africa.



Figure 4: 37 mm PVC filters post data collection event.

Analysis Method

A total of 50 PVC filters were used for air condition monitoring of the breathing zones of workers during the data collection event. Gravimetric analysis was performed, according to MDHS 14/4, on all the filters to assess the total mass of respirable dust to which the workers were exposed during their shift. Sample holders, specific to the filter size and cassette used during air sampling were used to secure the PVC filters in the sample compartment of a PerkinElmer Spectrum Two FT-IR. All background and sample spectra were retrieved using the data collection parameters outlined in Table 1. Background spectra were collected after every 5 samples using a clean, unused PVC filter from the same batch as the filters used for the personal air monitoring of the workers. Sample spectra were ratioed to

the background spectra of the clean PVC filters resulting in absorbance spectra.

Following FT-IR analysis, all sample filters were sent to a third-party laboratory for reference measurement following Method MDHS101/2 and NIOSH 7602 using X-Ray Diffraction (XRD) techniques, respectively.

A site-specific adjustment factor was determined using eight of the fifty filter samples. The adjustment factor was calculated using the FAST Mine-Specific Adjustment Tool provided with the FAST software developed by NIOSH. This adjustment factor, determined by inverse linear regression analysis, indirectly accounts for the presence of mineral interferents and their contribution to the infrared spectrum.

For the remaining 42 samples, which were not utilized in the calculation of the site-specific adjustment factor, peak area calculations were performed on the acquired sample spectra using an automated data analysis macro. The peak areas and associated baseline parameters are outlined in Table 2. Calculated peak areas and sample details including pump flow rate, cyclone type and flow duration were entered into the FAST software to calculate the silica mass concentration for each sample. The FAST software reports the quantified RCS mass in micrograms and the RCS concentration in units of micrograms per cubic meter ($\mu\text{g}/\text{m}^3$).

Parameter	Value and Unit
Resolution	4 cm^{-1}
Number of Scans	16
Spectral range	4000 – 400 cm^{-1}
Phase correction	Mertz
Apodization	Strong

Table 1: Instrument parameters used for data acquisition of samples analyzed using the At-Site EoS DoF FT-IR method for the monitoring of respirable dust samples.

Component	Left Limit (cm^{-1})	Right Limit (cm^{-1})	Base 1 (cm^{-1})	Base 2 (cm^{-1})
Silica	816	767	816	767
Kaolin	930	900	930	900

Table 2: Peak area calculations for components within the respirable dust samples to be imported to the FAST software.

Results and Discussion

Spectral features located at approximately 800 cm^{-1} and 780 cm^{-1} are due the Si-O-Si symmetric stretching vibration of quartz and can be used in the quantitative analysis of RCS in air monitoring samples. Kaolin, a soft white clay, is

a major interferent as it has an absorption feature located at approximately 790 cm^{-1} , and this must be considered in the analysis if present in the sample matrix. Figure 5 is a representation of the pure component spectra of quartz and kaolin and shows the difference between quartz and kaolin.

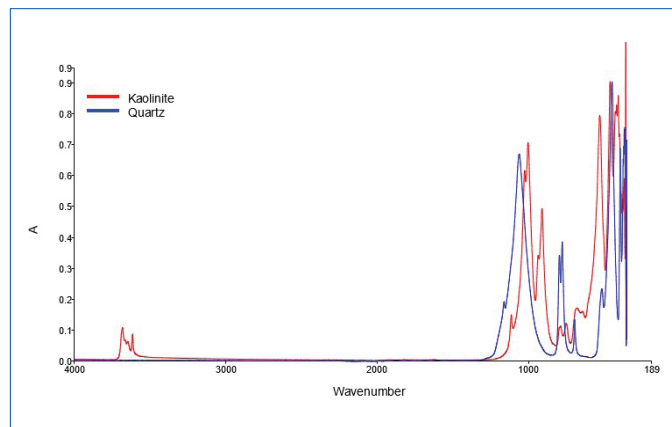


Figure 5: Pure component spectra for quartz and kaolin.

The DoF XRD results obtained by a third-party laboratory for reference analysis, following the MDHS101/2 method, indicated that 32 of the 50 PVC samples had RCS content below the detection limit. The limit of detection (LOD) as stated by the reference laboratory was 30 μg for the 37 mm PVC filters utilized during this study. Due to the low respirable silica concentration these samples were excluded from further analysis.

The remaining 18 samples, in which the XRD values were greater than the LOD, were further used to compare the At-Site EoS DoF FT-IR analysis method to those determined by XRD. Figure 6 shows a comparison of the RCS concentration as determined by the MDHS101/2 method and the At-Site EoS DoF FT-IR methods. A Spearman correlation coefficient of $r = 0.84$ indicates moderately strong agreement between the FT-IR and XRD values for RCS exposure.

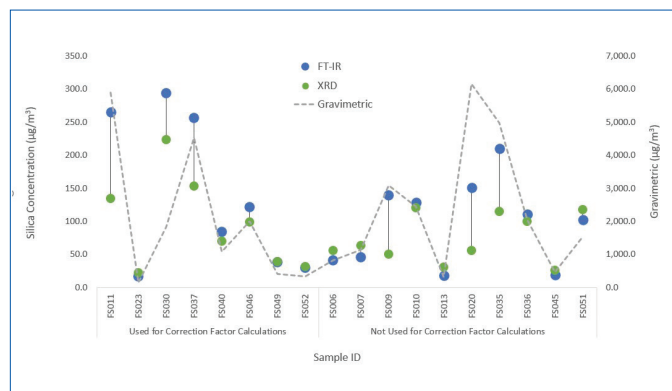


Figure 6: Line chart showing comparison between reference XRD and At-Site EoS DoF FT-IR values for RCS content.

The large offsets in predicted RCS concentrations for several of the samples are likely due to higher dust loadings on the PVC filter. Total respirable dust for all samples collected were determined using the MDHS14/4 method. A strong correlation exists (Pearson correlation coefficient, $R^2 = 0.90$) between the total dust loading and the difference between silica concentration determined by the At-Site EoS DoF FT-IR method and MDHS101/2 by XRD. However, this strong correlation between the dust loading and difference between estimated silica concentration values can be seen in Figure 6.

The site-specific correction factor was determined using the FAST software for 8 of the 50 samples and this was used for predicting the remaining samples having XRD reference values greater than the limit of detection. Figure 6 shows a correlation plot between the reference XRD values and the RCS concentrations as determined by the At-Site EoS DoF FT-IR method. Application of the site-specific correction factor results in an improvement of the correlation coefficient from 0.84 to 0.95 for uncorrected and corrected RCS mass concentration, respectively, indicating excellent agreement between the values.

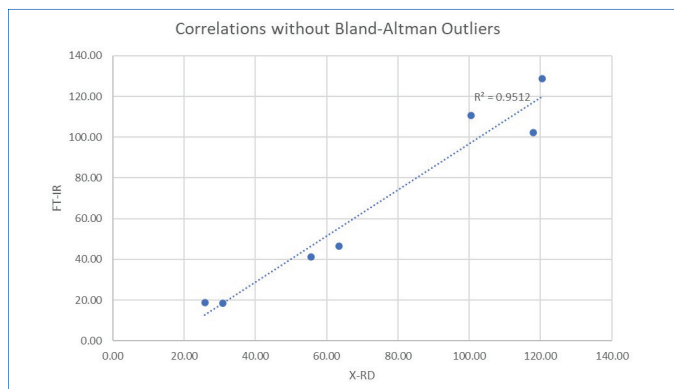


Figure 7: Correlation plot showing the agreement between the reference XRD value and silica concentration determined by the At-Site EoS DoF FAST method following application of a site-specific correction factor.

In addition to reference measurements by XRD according to MDHS101/2, reference measurements were conducted following NIOSH 7602 using FT-IR and the analysis of a KBr pellet. A chart is presented in Figure 8 which compares the 3 measurement techniques for 7 samples remaining following application of the site-specific correction factor. All the techniques follow similar trends across the presented datapoints and highlight the ability of the At-Site EoS DoF FAST method to be used for monitoring of RCS dust.

It is important to note that the At-Site EoS DoF FAST method for the analysis of respirable dust samples will not completely replace the need for reference samples to be analyzed according to established reference techniques. This method is complimentary to existing International Organization for

Standardization (ISO) accredited analysis methods. It is recommended that 20% of all analyzed samples be analyzed by an ISO 17025 accredited laboratory for validation.

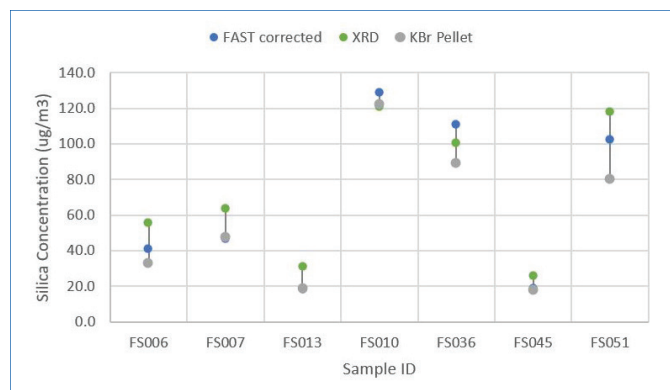


Figure 8: Chart comparing the three measurement techniques: At-Site EoS DoF FAST, XRD following MDHS101/2 and FTIR KBr pellet according to NIOSH 7602.

Summary

At-Site EoS DoF FT-IR analysis for RCS gives industrial/occupational hygienists the ability to respond the same day to potential overexposures allowing for more accurate record keeping of exposure events. Third party laboratories typically have turnaround times ranging from a few days to several weeks which can greatly hinder an overexposure investigation.

At-Site EoS DoF FT-IR analysis for RCS combined with FAST software provides users with an accurate tool that enables rapid quantification of RCS on-site thereby omitting the potentially long turnaround times associated with off-site analysis. The timely information provided, can help employers to control the risk of exposure more effectively to RCS in the workplace by taking action as soon as these risks present themselves. The FAST software not only computes the amount of silica present within the sample filter and the corresponding exposure level but also acts as a single point for storing critical information such as worker and location details, worker tasks during sampling events, and sampling media information. The ability of FAST data to be shared quickly across devices gives industrial/occupational hygienists the tools they require to promptly deal with overexposures to RCS dust and prevent future overexposures.

Several studies have shown that FT-IR spectrometry has the potential to reasonably estimate the RCS exposure of workers, in an EoS DoF method and that the PerkinElmer Spectrum Two is capable of generating precise and reproducible DoF analysis results from respirable dust samples.

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