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Research Article

Respirable Silica: An Analysis of Recent Advances

Michael Shivers, Nicole Betson, Joseph Kazery, Tanisha Hinton, Ramzi Kafoury, Paul Tchounwou

[1]Jackson State University 1400 John R. Lynch Street Jackson, Mississippi 39217

Correspondence: Ramzi Kafoury

Abstract: Prevention and reduction of anthropogenically released greenhouse gasses and respirable particulate matter has enhanced health with environmental monitoring. It has shown exposure to carcinogens. Air quality analysis showed silica, polycyclic aromatic hydrocarbons, sulfuroxides, nitroxides, and ozone were associated with respiratory diseases in urban, residential, street level areas near windows. Moreover, validation with measurements of temperature, humidity, climate change, or energy production and consumption may show more silica associated with public health.

1. INTRODUCTION

Silica, also known as silicon dioxide ($SiO2$), is a white, solid compound comprised of the most ubiquitous elements on earth, silicon (Si) and oxygen ($O2$). It is the most abundant compound in the earth's crust, which constitutes 59% of its total composition (Zhang, et al. 2016). The chemical groups of $SiO2$ include Silicon 14 and Oxygen 16 with electron configurations [Ne] 3s2 3p2 and [He] 2s2 2p4, respectively. Its density is 2.4 g/cm3 and molar mass is 59.96 g/mol. The melting point is 1600°C and has a boiling point of 2230°C. It does not react with water, and does not decompose with heat but, it is insoluble in all acids with the exception of hydrogen fluoride (HF) (Boule et.al 05).

Silicon occurs in nature combined with oxygen, in the form of silicon dioxide, and with oxygen and several metals, in the silicate form, but is never found isolated (Barrett, 09). The quartz is very common and it can be found in granite, sand and sandstone. Crystalline silica is considered as one of the most common and serious occupational hazards to workers' health (Barrett, 09). Crystalline silica is a very common mineral and is often referred to as quartz.

Construction sites with silica in soil, sand, concrete, masonry, rock, granite, and landscaping materials decrease its size. Dust created by cutting, grinding, drilling or otherwise disturbing these materials generally contains crystalline silica particles. Coal mine dusts were collected in coal mining processes with respirable particulate matter and showed two percent silica quartz (Soo, et al. 2016). These dust particles are very small, and thereby respirable. Silica dust causes lung disease and lung cancer. More than 50 µg m-3 of airborne silica dust over an 8 hour period has been reported to cause adverse health effects (Tao, 2010). Furthermore, exposure to silica nanoparticles with diameter 30 nm reduced function of liver and blood cells (Isoda, et al. 2013; Kusaka, et al. 2014). Near infrared reflectance spectroscopy of grass near coal fired power plants showed silica absorbed in plants and was condensed hydrated orthosilic acid $Si(OH)4$ (Smis, et al. 2014). The volatilization reactions of silica in water-vapor environments most likely to occur are:

$$SiO2\,(s) + H2O(g) = SiO(OH)2(g) \qquad (1)$$

$$SiO2\,(s) + 2H2O(g) = Si(OH)4(g) \qquad (2)$$

$$2SiO2\,(s) + 3H2O(g) = Si2O(OH)6(g) \qquad (3)$$

Direct high-pressure mass spectrometry at low pressure in a 22mm ID fused quartz furnace tube, with oxygen and water vapor identified volatile hydroxides of silica by mass spectral intensity and showed $Si(OH)3+$, $Si(OH)4+$, and $SiO(OH)+$ (Opila, et al. 1997).

The main routes of silica exposure are inhalation, ingestion, skin contact and eye contact. Inhalation of silica at high concentrations and can irritate the nose and throat. Dermal contact with silica does pose a health risk with the exception of dermal abrasion under turbulent conditions. Eye contact may cause slight irritation as a "foreign object". Tearing, blinking and mild temporary pain may occur as particles are rinsed from the eye by tears (Cerasela Daniela., 2017). Ingestion is not reported to cause serious harm, however, long-term (chronic) exposure is very toxic. In regards to inhalation, silica can cause lung damage when the dust is inhaled. Symptoms may include shortness of breath, chronic cough and weight loss. There may also be a decrease in lung function and ability to perform some physical activities. In severe cases, significant damage to the heart has been found, in addition to death from heart failure (Cerasela Daniela., 2017).

In addition to localized health effects, $SiO2$ exposure can result in systemic effects as it is a known carcinogen that causes lung cancer. The International Agency for Research on Cancer (IARC) classifies it as a group 1- carcinogenic to humans. The American Conference for Governmental Industrial Hygienists (ACGIH) classified it A2, suspected human carcinogen; while the Environmental Protection Agency (EPA) classifies it as a known human carcinogen (Zhang et., al 2016).

A. II. TRADITIONAL METHODS

As seen in many studies a flow rate aerosol sampler is the instrument commonly used to collect respirable dust for quantitative analysis (Chisholm et al. 2013; Kauffer et al. 2002; Lee et al. 2010). These typically consist of a battery-operated pump connected to a cyclone sampler with a filter contained in a cassette (SKC 2011). The cyclone sampler separates dust into a variety of respirable fractions usually less than 10 micrometers AED (Aerodynamic Equivalent Diameter). This removes larger unwanted particles.This is achieved by aerosol particles moving across a curved airstream due to particle centrifugal force. With larger diameter particles have a greater centrifugal force allowing greater deposition on the internal cyclone walls increasing cyclone collection (Moore & McFarland 1993). After the cyclone, the respirable samples are collected in a 37 mm, polyvinyl chloride (PVC) filter that is situated in a cassette holder. The filter should have the pore size of 5um and produce low amount of residue when washed (NIOSH 2003).When other types of filters are used such as cellulose acetate with a 0.8 um pore size it is typically for other respirable dusts (Bratveit et al. 2003). However, other filter sizes such as the 25 mm PVC filter have been shown to just as effective (Amran et al. 2016). Variations in the flow rate allows for separation of particles with a specific diameter. For silica, the flow rate should be 1.2-2.8 L/min for a 4 to an 8 hour workshift (Kauffner et al. 2002; Foster & Walker 2000; Braveit et al. 2003; NIOSH 2003). The filters used, with the collected samples, are then ashed, digested, or otherwise prepared based on the analysis methods used.

The three main traditional methods for determining respirable silica: colorimetric, X-ray diffraction, and an infrared method (Chisholm et al. 2013; Harper et al. 2014). In 2000 the American Conference of Governmental Industrial Hygienists (ACGIH) lowered the Threshold Limit Value (TLV) of respirable silica to 0.05 mg/m3 (Wickman & Middendorf 2002) and in 2006 furthered lowered it to 0.025 mg/m3 for an 8 hour time-weighted average (Harper et al. 2014; Lee et al. 2010). With these changes a greater sensitivity would be preferable to monitor concentrations below the current TLV where it is more fitting for a part-time shift less than 8 hours (Chisholm et al. 2013; Dahmann et al. 2008). The colorimetric method is a wet chemical method and is the oldest that can be found in the NIOSH Manual of Analytical Methods. In this procedure a quartz sample has been ashed after digested phosphoric acid which removes all forms of silicon material except the quartz. This method uses the absorption of a silicomolybdate complex for a visual analysis and has a 0.010 mg/m3, 10 ug, limit of detection(LOD) (Chisholm et al. 2013).

The benefit from using this method is its low LOD (Chisholm et al 2013). However, it seems that the disadvantages far outweigh the advantages. In fact, determining the amount of silica by photometric analyses has been regarded as unreliable for many years (Wilson & Skinner 1960), and has been described as time-consuming (Govett 1961) and labor-intensive (Chisholm et al. 2013).

It has been observed that many results were not reproducible if pH fluctuated or if reagents such as ammonium molybdate were allowed to stand too long (Wilson & Skinner 1960). The accuracy of this method also comes into question as a disadvantage if other forms of silica are present and to the skill of the analyst executing the procedure (Chisholm, et al. 2013). Changes in OSHA policy lead to changes in PEL down to 0.05 mg/m3 (Lee, et al. 2010). This updated PEL calls for better precision and per Chisholm et al. that with inherent limitations it is not likely that this method could be altered to lower its LOD (2013). This method was used extensively up into the 1990s and has since then been phased out (Dahmann, et al. 2008; Harper et al. 2014).

X ray diffraction is an analytical method used for crystalline silica that is not a chemical or elemental analysis. It instead is based on the atom position of the crystalline lattice as well as the distances between planes of atoms. The diffraction pattern is unique to each crystalline structure, and each polymorph of silica has a slightly different structure (Kauffer et al. 2002; Stone et al. 2016). Differences in particle size distribution has also shown to affect diffractometer response (Gordon & Harris 1955; Stone, et al. 2016) and the volume median diameter of samples can be measured by the Coulter counter technique (Ito et al. 2004).

Kauffer et al. (2002) used a Philips PW 1729 powder X-ray diffractometer and calibrated with the four strongest lines (101, 100, 112, 211) from each filter standard after linear background corrections were made . Golbabaei et al. (2004) used a Siemens Model D5000 diffractometer using 2θ peak at 26.686. Stone et al. utilizes a Rigaku DMAX Diffractometer. A list of primary, secondary, and tertiary peaks angles (2θ) for quartz, cristobalite, and tridymite are available in the NIOSH Manual of Analytical Methods (NMAM), fourth edition (NIOSH 2003). Parameters for slits varied slightly with each study.

Collections on organic membranes such as polyvinyl chloride (PVC) or cellulose ester produced a high amount of background scatter as a continuous weak diffraction pattern. This problem was corrected by Bumsted (1973) with the use of silver filters (Foster & Walker 1984; Tossavainen 1979). Polyvinyl chloride may be ashed then transferred to silver membrane filters (NIOSH 2003) or dissolved in tetrahydrofuran and evenly dispersed to silver membrane for X ray diffraction (Bratveit et al. 2003; Stone et al. 2016; Yassin et al. 2005).

X-ray diffraction peaks are sensitive to each crystalline structure (Chisholm et al.2013; NIOSH 2003). This is the method used by Occupational Safety and Health Administration (OSHA), method ID-142 , and is highly effective for determining the polymorphs and quantifying crystalline silica with industries that produce a wide variety of dusts (Stone et al. 2016). A specific structure allow interference to be easily corrected. This is an advantage over the colorimetric method that only quantifies quartz. The LOD has been reported in one study as being 10ug, who was using NIOSH method 7500 method that is similar to the OSHA Method (Lumens & Spee, 2001). This would not be considered advantageous with the PEL of 5ug. However, according to other studies and the National Institute for Occupational Safety and Health (NIOSH), this method should provide a LOD of 5ug for quartz, crystobalite, and tridymite (Chisholm et al. 2013; NIOSH 2003; Stone et al. 2016). This method is already very efficient and has been discussed by Chisholm et al. that X-ray diffraction could improve if more X-rays could be generated or increase the scattering efficiency of quartz (2013).

The main drawback is the X-ray diffractometer (Chisholm et al. 2013). But as for the method, transfer of contents, size of silica, or other crystalline substances may have an effect. The transfer of contents from the cyclone is unreliable is sample is spilled. The size distribution of silica particles have an effect in that the smaller diameter silica in our respirable range is measured less accurately than the larger particles (Chisholm et al. 2013; Kauffer et al. 2002). There are some materials that have a similar pattern to crystalline silica such as feldspar, graphite, or kaolinite to name a few. These other substances typically only interfere with primary peaks, but not as much with secondary and tertiary (Stone et al. 2016). This issue can be overcame by using multiple peak angles.

Infrared spectrometry uses a potassium bromide pellet to hold the sample in the infrared beam. The pellet is made from the collected respirable dust that has been ashed, mixed with potassium bromide or cesium bromide (Foster & Walker 1984), and pressed with a die (NIOSH 2003). According to Kauffer et al. there are other techniques aside from KBr pellets others worked on filters either by air or liquid filtration (2002). Crystalline silica methods can be found in NMAM 7602 and 7603 (Chisholm et al. 2013). Kauffer et al. (2002) utilized a Nicolet Magna 560 infrared spectrometer exploring the spectral range 6400 to 200 cm-1. Where Foster and Walker (1984) scanned from 400 to 1500 cm-1. The analytical bands were found at 798, 780, 695, 398 and 374 cm–1 were used by some (Kauffer et al. 2002) and 799, 780, and 695 cm-1 Foster & Walker 1984). According to Beer's Law the peak intensity, which may be higher or wider, is proportionate to the mass of the absorbing molecules (Chisholm et al. 2013).

The LODs have varied in recent studies of 10 to 5 ug for method NMAM 7602 and 30 to 10 ug from method NMAM 7603(Chisholm et al. 2013). Which at least is a comparable to X-ray diffraction and at best the lowest detection limit yet. Ainsworth (2005) has even reported a 4 ug LOD using the MSHA P-7 method. This is beneficial being below the ACGIH current TLV. An alternative advantage of infrared spectrometer is the low cost (Chisholm et al. 2013). Chisholm et al. (2013) has proposed a method to increase sensitivity by increasing the peak height of absorbance value that the sample is measured. The spectral width of a given peak is the only feature of the vibrational absorbance spectrum that can be modified. This make wider bands narrower and more intense which is a temperature dependent process that would be more sensitive at lower temperatures. Performing the infrared absorbance measurement at 77 K rather than 300 K, increasing signature bands 50%, increasing sensitivity 25%.

This method is relatively time consuming and the preparations of the pellet may be open to possible errors by the analyst, being transferring or other preparation issues. Also, too high a mass collected cannot be analyzed which is true for both infrared and X-ray diffraction. Other materials such as kaolin being commonly found in dust is a source of interference with either quartz or cristobalite, but there are other bands that can be used or corrections. Kaolin's interfering peaks between 754 to 795 cm-1 can be removed from the spectrum along with muscovite, nepheline, feldspar, oxides of iron or graphite, and others that commonly found in ceramics, mining, and quarries. For example, zircon having a strong 620 cm-1 peak engulfs the 622 cm-1 cristobalite band requiring an alternative band to be used (Chisholm et al. 2013; Dahmann et al. 2008; Foster & Walker 1984; NIOSH 2003). Also, the lower temperature method of increasing sensitivity as mentioned by Chisholm et al. (2013) has not been thoroughly tested using a dust mixture.

Overall, both X-ray diffraction and infrared spectroscopy seem to be satisfactory methods for determining the concentration silica at current NIOSH standards. Both methods are very comparable to each other in accuracy (Dahmann et al. 2008). However, should standard TLV be lowered again, it would be beneficial to utilize infrared spectrometry since it has the capability to measure a lower LOD. The colorimetric method may still have its place in academics or for comparison studies, but other than that is obsolete.

B. III. LITERATURE REVIEW

There are primarily four main technological equipment available for detecting and analyzing silica particle, there are: XRD, IR, UV-VIS and ICP-MS (spICP-MS). Analysis of crystalline silica in airborne dust samples collected on filters using a size selective sampler (i.e. a 10 mm nylon cyclone) is simple to perform routinely by instrumental methods such as XRD [National Institute for Occupational Safety and Health (NIOSH, 1994a)], IR (Dodgson and Whittaker, 1973; NIOSH, 1994b) and the colorimetric method employing UV-VIS (NIOSH, 1994c). However, there are significant problematic areas that need to be addressed and improved. The pressing issues that are present in the latter methodologies for detecting silica particles and analysis are:

1. The determination of crystalline silica (α-quartz) in bulk samples has not been developed
2. The development of a detailed protocol for analyzing bulk samples has not been reported
3. The use of an appropriate calibration standard.

4. A detailed quality control of nanoparticle size analysis methods
5. Great need for sophisticated instrumentation and more sensitive analytical techniques
6. Obstacles arising from relatively high particle number concentrations and high backgrounds of dissolved analytes.

Nevertheless, there are new or novel methodologies on the rise that can address issues with the use of traditional methodologies and technological equipment used. The four main novel methodologies and technological equipment used are:

Fourier transform infrared spectrophotometry

ERM-FD102

Microsecond technique

Post- Silicon works

C. 3.1 Fourier transforms infrared spectrophotometry

Dust samples that contained crystalline silica in ambient air were collected by size using a selective sampler on filter paper. The selective sampler is 10mm nylon cyclone to routinely perform simple instrumental methodologies such as: IR (Dodgson and Whittaker, 1973; NIOSH, 1994b), colorimetric method employing UV-VIS (NIOSH, 1994c) and XRD (National Institute for Occupational Safety and Health (NIOSH, 1994a).

However, the latter does conduct bulk sampling in protocol. In this paper, we shall implore and describe an approach analytically for measuring the crystalline silica of samples in bulk. With subsequent analysis of the finer fraction, sample preparation via grinding and sieving are the three methodological processes involved in bulk sampling analysis by FT-IR (Fourier transform infrared spectrophotometry). The FT-IR has many functions that are tremendously beneficial which are: applicability to analyze bulk samples, different fractions can be observed portraying the degree of difference, determination of an array range of method but most importantly it can measure crystalline silica of 0.1% by weight in bulk samples.

The determination of bulk samples of crystalline silica has now been realized with the advanced, Fourier transforms infrared spectrophotometry. The diameters of the particle sizes are <10 µm in diameter, which can be sieved based on the respective sizes. Before sieving process the homogenizing of bulk sample is required. Sieving is a vital technique. Without sieving process of the ground sample it shall be inappropriate since there is a clear relationship between sample that is ground unsieved and the <10-µm fraction.

D. 3.2 ERM-FD102

The Institute for Reference Materials and Measurements of the European Commission's Joint Research Centre developed and produced an emerging certified reference material for the nanoparticle size analysis methods for quality control. This novel technology is called ERM-FD102 (ISO Guide 34, 2009). A mixture of silica nanoparticle populations that consist of an aqueous suspension based on origin and distinct particle size. Interlaboratory comparison study is very vital in its characterization. Data sets received must be scrutinized and indicative values for the different method- defined equivalent diameters, which are specific dynamic scattering light. A common particular challenge in the ERM-FD102 is the value assignment due to the fact that concept of metrological inputs shall not be uniformed across all laboratories. Inn addition, the measurements of uncertainty are of question (S.B. Rice et.al 2013).

E. 3.3 spICP-MS

Sophisticated instrumentation and analytical techniques that are more sensitive is in great need. Nevertheless, the spICP-MS seems to be a promising powerful tool for not only the characterization of sample size but also for detection in environmental samples. This technology has been designed to improve analysis of an even greater breadth samples environmentally via the working resolution enhancement, increasingly complex matrices and utilization of the microsecond dwell times (Leitch 2012, Peer 2007). Dissolved analyte tends to produce a high-resolution background and high particle number concentration causing problematic scenario when it comes to data analysis. On the contrary, spICP-MS overcome the latter issue via dual element detection (Anker 2008).

Dual element detection provides more accurate representation of not only engineered number but also size in solution. This powerful tool does not need the excessive sample preparation in order to be able to distinguished naturally occurring particle. spICP-MS overcomes majority of issues via the development of the Nano software. The disadvantage of spICP-MS is that data may be lost that are at the edges of the pulse to the signal of the background. Consequently, the latter shall be excluded from the intensity of the particle holistically.

Additionally, the count generated by the sample has a small reading (2-4 reading) to dwell time window. Thus, with the reduced dwell time the count intensity shall dramatically be reduced. Accordingly, the intensity within the sampling event will also decrease between sampling events. As a result, even though resolution between particle events increases. The overall detection limit in regards to size increases (Tao 2010). Further development of this technique in readdressing the sensitivity issue is at work but it is still the premiere technique in characterization and detection of silica particle.

F. **IV. Post Silicon**

Validation of post-silicon is one of the pressing issues in effectively detecting silica. The analysis must be free of bugs in the integrated circuits in any technological machine used in not only detecting silica but also analyzing silica. Sometimes after manufacturing bugs are present at it's highest in the integrated circuit (Abramovici 06). As a result, detection of the bugs are difficult to be rectified. An exciting major innovations in electric design automation offers an emerging research area to address the latter issue mentioned, Post-Silicon. Challenges and recent advances in technology shall be implored in this section of the paper.

The verification after the real silica must be in place is known as the Post-Silicon Validation. This technological equipment was designed in such way that verification of each phase of development must be undergo (Bardell 87). The output produced must be in understandable format for tester to analyzed. It is formatted and converted differently from original format through output stimulation.

There are three primary components that involves in the process of Post-Silicon Validation. The three types of basic tests those devices needs are: Per Pin Testing, Parametric Testing, and Functional Testing. The Per Pin Testing is the part of the device that must focus on circuitry local. Illustrations of the Per Pin Testing are: Input/output impedance tests, continuity tests and leakage tests. Parametric Testing pertains to the values of the device "parametrically". For example, Gain test, SNR performance test, and icc tests (Barrett 09). Lastly, most active part of the device is the, Functional testing; In addition, the functionality of the device operating in the environment naturally would exist in final product.

G. 4.1 Brief Synopsis of how Post- Silicon works:

Input for post silica validation often referred as the file generated through stimulation. The machine consists of an external value change dump that captures pertinent information from all input ports. The direction of information, strength and value at each transition are captured in the external value change dump (Bayazit 05, Barrett 09).

However, the external value change dump output can be very difficult for tester to comprehend. Thus, it is imperative to undergo a conversion process so that the tester can comprehend (Boule et.al 05). This conversion process is often referred to as the drive/ receive formats. Compartmentalization of each time slot that consists of specific information must be in understandable format. Hence, denotation of each time slot is executed, vector. The inbuilt mechanism to sample output ports must be compared against a declared pass/fail; consequently, this is one of the primary disadvantages of this method (Dahlgren 03).

H. V. CONCLUSION

Prevention and reduction of anthropogenically released greenhouse gas and respirable particulate matter has enhanced health with environmental monitoring and reduced exposure to carcinogens. Air quality analysis showed silica, polycyclic aromatic hydrocarbons, sulfuroxides, nitroxides, and ozone were associated with respiratory diseases in urban, residential, street level areas near windows.

Moreover, coal mine dust collected during coal mining showed samples contained increased silica quartz with ten nanogram diameters (Soo et al, 2016). Exposure to silica nanoparticles with diameter 30 nm reduced function of liver and white blood cells (Isoda et al, 2013; Kusaka et al, 2014). Silica absorbed in plants is condensed hydrated orthosilic acid Si(OH)4. Grasses near coal fired power plants showed increased absorption of silica in near infrared reflectance spectroscopy (Smis et al, 2014).

Validation with temperature, humidity, climate change, energy production and consumption may show silica associated with public health. The US Occupational Safety and Health Administration OSHA regulated permissible exposure limit to 0.05 within an action level of 0.025mg /cubic meter (OSHA, 2014). The most common sampler is the 10-mm nylon cyclone with a sampling pump at 1.71 L /min.

Calibration of high flow rate sample collection units enhanced limits of detection and limit of quantification for respirable dust mass concentration (Lee, et al 2016). Area samples were conducted at mining and refinery, concrete drilling and construction, and bricklayer training sites with reduced spatial variability of a stationary Lippman-type sampling apparatus.

Silica reinforced polymers are used for their porosity and surface area made of silica and oxygen. Silica reinforced foams polymers are used in electrical and fiberoptic cables, home or automobile insulation and sealants, furniture. Thermal resistance of silica has applications with material complexation in nuclear power plants, and outer space components for structures. Radiation transformed silica reinforced polymers and showed enhanced porosity, and reduced stability of structures measured with Scanning Electron Microscopy (Fang et al, 2017).

Industrial hygiene laboratories commonly used one of three analytical techniques for detection or quantitation of respirable crystalline silica during 1990 and 2001. Silica such as in coal mine dusts or respirable particulate matter has been studied extensively and includes X-ray Diffraction XRD, Infrared spectrometry IR, and Colorimetric spectrophotometry.

However, colorimetric spectrophotometry used during April 1990 to April 1998 has since showed poor lower detection limits (Harper et al 2014). During 2006 American Conference of Governmental Industrial Hygienists ACGIH recommended an advisory limit of 0.025mg/m^3 with 8-hour time-weighted average. Current permissible exposure limits PEL are 0.05mg/m^3. To reduce occupational exposures to respirable particulate matter, lower detection limits detect identify, monitor, and remove potential exposures.

Proficiency Analytical Testing with accredited and non-accredited labs used referenced methods for XRD, IR, or colorimetric analysis of silica in coal mine dusts. Sampled coal mine dusts CMD, talc, CMD plus talc, or calcite were included for silica analysis, and XRD resulted in more precise and accurate results with both accredited and non-accredited labs (Harper et al 2014).

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