Gijima
Technology People

SAIOH Mpumalanga Information Session

Silica

27 May 2011

Agenda

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What is Silica?

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- Silica refers to the chemical compound Silicon dioxide (SiO_2).
- One Silicon atom, bonded to two Oxygen atoms – meaning it is an oxide of Silicon.
- Nothing else – but also much more.
- A natural chemical compound formed through petrochemical (geological) processes is called a mineral.
- It does exist naturally as mineral Silica polymorphs (minerals of the same composition but with different crystal structures) as well as non-crystalline forms.
- It is also produced synthetically.

In the Beginning…

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Silica consists of Silicon and Oxygen

- Silicon and Oxygen:
  - Silicon is the second most abundant element (after Oxygen) in the earth's crust by mass.
  - Silicon very (extremely) rarely occurs in its pure elemental form in nature.
  - Not surprisingly though, it is most commonly encountered in combination with Oxygen (the other most abundant element in the earth's crust) as Silicon oxides

Silica – Natural forms

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- Crystalline Silica – mineral polymorphs.
- Amorphous Silica – volcanic glass and Diatomaceous earth

Crystalline Silica - natural

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- Crystallization occurs as a result slow cooling of magma, which has contained “bubbles” of Silica (Silicon dioxide), that has formed through complex petrochemical reactions.
- The slower the cooling down process, the larger the size of crystals.
- Crystalline silica is thus extremely common in igneous rocks, or sands formed from the weathering of such igneous rocks.
- The morphology (shape/3-dimentional appearance)of the Silica crystal is a function the temperature and pressure that prevailed when it was formed (crystallization occurred).

Crystalline Silica - natural

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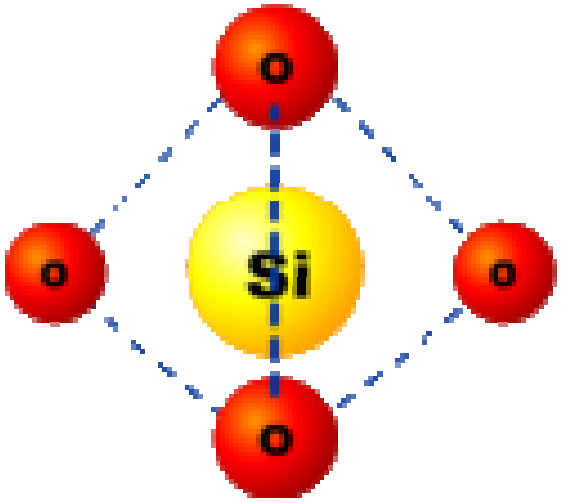
- Although the chemical formula of crystalline Silica is SiO_2, its structure formula is SiO_4 - SiO_4 tetrahedra:



Crystalline Silica - natural

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Crystalline forms/Polymorphs:

- The temperature and pressure at which the Silica crystal formed, determines its polymorphous structure:
  - α-Quartz has a Oxygen-Silicon bond length of 161 pm and a Si-O-Si angle of 144°
  - whereas in α-Tridymite has a O-Si bond length in the range 154–171 pm and a Si-O-Si angle between a low value of 140° up to 180° in β-Tridymite.

Crystalline Silica - natural

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Most common Forms/Polymorphs of crystalline Silica.

- α-Quartz, is the second most abundant mineral in the earth's crust (after Feldspar – another silicate mineral). It is the most stable form of crystalline Silica.
- Tridymite is a high-temperature polymorph of crystalline Silica. It is not nearly as abundant as Quartz. It could be more abundant where Quartz or even amorphous Silica has been exposed to very high temperatures for extended periods of time (such as refractory lining of furnaces).
- Cristobalite is a high temperature/low density polymorph of Quartz and exists in the earths crust or on the surface outside of its thermodynamic stability range because of the transition from Cristobalite to Quartz or Tridymite. Cristobalite is stable only above 1470 °C. It is fairly rare, but can be found in the precious mineral known as Opal.
- Other crystalline forms of Silica (high pressure polymorphs) include Seiferite, Stishovite and Coesite (their chemical formula's are however not strictly SiO_2)

Crystalline Silica - natural

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Ores of crystalline Silica:

- Tripoli, also known a Novaculite, is a form of microcrystalline or cryptocrystalline Quartz (magma that was rich in Silica that cooled rapidly to produce very small crystals).
- Most igneous rocks and sand/dirt derived from the weathering thereof.
- Sandstone
- Quartzite (metamorphisised Sandstone - the Vaal Reef; our richest Gold ore).
- Flint (or Flintstone) is a hard, metamorphisised, sedimentary, cryptocrystalline form of Quartz. It is another variety of Chert. Other varieties include Grint, Jasper, Onyx, etc.

Crystalline Silica - natural

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Variations in crystalline Silica/Quartz:

- Impurities in the Quartz crystal, creates color variations, making it very popular semi-precious gemstones:

Crystalline Silica - natural

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Crystalline Silica - natural

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Chalcedony	Cryptocrystalline quartz and moganite mixture. The term is generally only used for white or lightly colored material. Otherwise more specific names are used.
Agate	Multi-colored, banded chalcedony, semi-translucent to translucent
Onyx	Agate where the bands are straight, parallel and consistent in size.
Jasper	Opaque cryptocrystalline quartz, typically red to brown
Aventurine	Translucent chalcedony with small inclusions (usually mica) that shimmer.
Tiger's Eye	Fibrous gold to red-brown colored quartz, exhibiting chatoyancy.
Rock crystal	Clear, colorless
Amethyst	Purple, transparent
Citrine	Yellow to reddish orange to brown, greenish yellow
Prasiolite	Mint green, transparent
Rose quartz	Pink, translucent, may display diasterism
Rutilated quartz	Contains acicular (needles) inclusions of rutile
Milk quartz	White, translucent to opaque, may display diasterism
Smoky quartz	Brown to gray, opaque
Carnelian	Reddish orange chalcedony, translucent
Dumortierite quartz	Contains large amounts of dumortierite crystals

Crystalline Silica - natural

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Where could you encounter crystalline Silica

- Crystalline Silica is fairly hard (resistant to weathering) and will thus concentrate in sand, soil and dirt; any process where such dust is generated.
- Any process where natural rock is mechanically or otherwise broken down – mining and other mineral processing processes, or where rocks/minerals are handled.

Amorphous Silica - natural

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- **Volcanic glass**
  - Lava rich in Silica that cooled too rapidly to result in any form of crystallization (mineral called Obsidian).
- **Diatomaceous earth**
  - Deposits of the skeletons of diatoms (aquatic micro-organisms with Silica skeletons).

Amorphous Silica - Synthetic

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- **Silica fume**
  - Rapid cooling of gas phase SiO_2, as a result of the melting of crystalline Silica (furnace/smelting processes). *Not synonymous with fumed Silica.*
- **Silica gel**
  - Chemically produces amorphous Silica (used as a desiccant).
- **Fumed Silica**
  - Also known as pyrogenic Silica because it is produced in a flame
  - consists of microscopic droplets of amorphous Silica fused into branched, chainlike, three-dimensional secondary particles which then agglomerate into tertiary particles.
- **Fused Silica (Silica glass)**
  - Glass produced from Quartz, using the melt-quench method. Used in semi-conductors, Halogen lams, laboratory glassware, lenses.

Crystalline Silica - Synthetic

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- **Silica nano-particles**
  - Synthetic cultured nano crystals (extremely toxic)

Health Hazards – crystalline Silica

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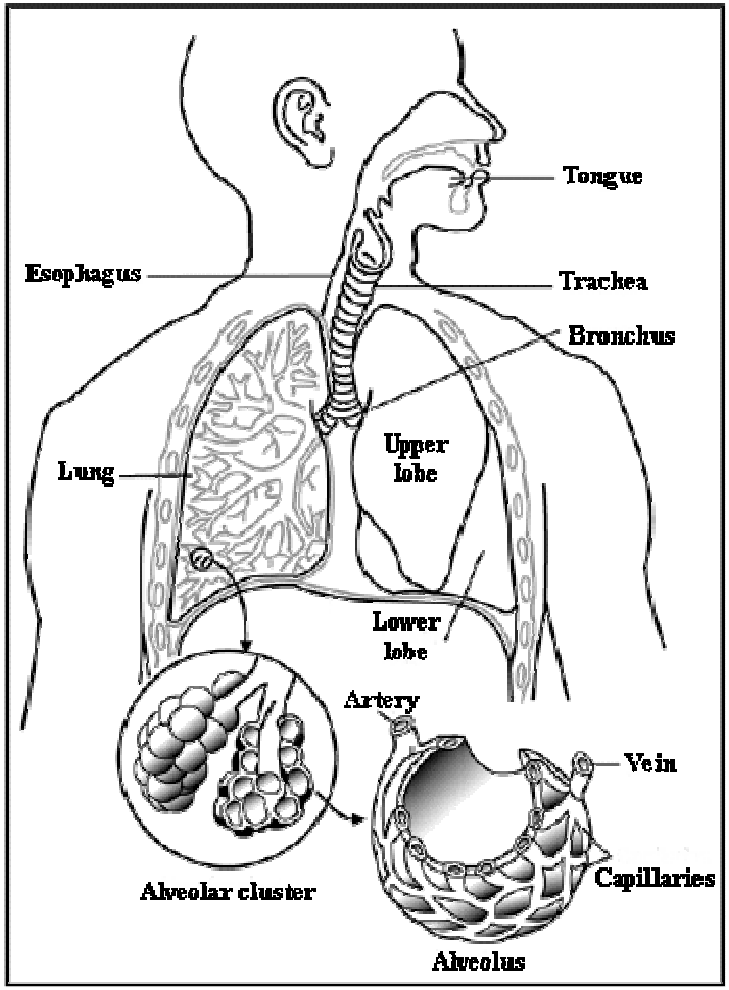
- **Respirable Particle deposition:**



Health Hazards – crystalline Silica

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- **Silicosis:**
  - Silicosis is a pneumoconiosis, that is usually caused by inhaling crystalline free Silica (Silicon dioxide) dust and is characterized by discrete nodular pulmonary fibrosis and, in more advanced stages, by conglomerate fibrosis and respiratory impairment.
  - Silicosis is the oldest known occupational lung disease. Is documented as occurring in antiquity, for example in Egyptian mummies.

Health Hazards – crystalline Silica

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- **Stages of Silicosis:**
  - Chronic silicosis, which usually occurs after 10 or more years of exposure to crystalline Silica at relatively low concentrations
  - Accelerated silicosis, which results from exposure to high concentrations of crystalline silica and develops 5 to 10 years after the initial exposure
  - Acute silicosis, which occurs where exposure concentrations are the highest and can cause symptoms to develop within a few weeks to 4 or 5 years after the initial exposure.

  - *For nano particles, the same effects are expected, but much quicker and at much lower concentrations*

Health Hazards – crystalline Silica

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- **Silicosis - Complications**
  - Silicosis (especially the acute form) is characterized by shortness of breath, fever, and cyanosis (bluish skin); it may often be misdiagnosed as pulmonary edema (fluid in the lungs), pneumonia, or tuberculosis.
  - Severe mycobacterial or fungal infections often complicate silicosis and may be fatal in many cases.
  - Fungal or mycobacterial infections are believed to result when the lung scavenger cells (macrophages) that fight these diseases are overwhelmed with silica dust and are unable to kill mycobacteria and other organisms.
  - About half of the mycobacterial infections are caused by ***Mycobacterium tuberculosis,*** with the other half caused by ***M. kansasii*** and ***M. avium-intracellular***.
  - ***Nocardia*** and ***Cryptococcus*** may also cause lung infections in Silicosis victims.
  - Investigations usually show the lungs to be filled with Silica crystals and a protein material

Health Hazards – crystalline Silica

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- **Silicosis – Diagnosis (Chest X-Rays)**
  - Simple Silicosis - multiple, small, rounded or regular opacities on the chest x-ray, classified as category 1, 2, or 3 according to their profusion
  - Complicated Silicosis - opacity > 1 cm in diameter on a background of category 2 or 3 simple silicosis

Health Hazards – crystalline Silica

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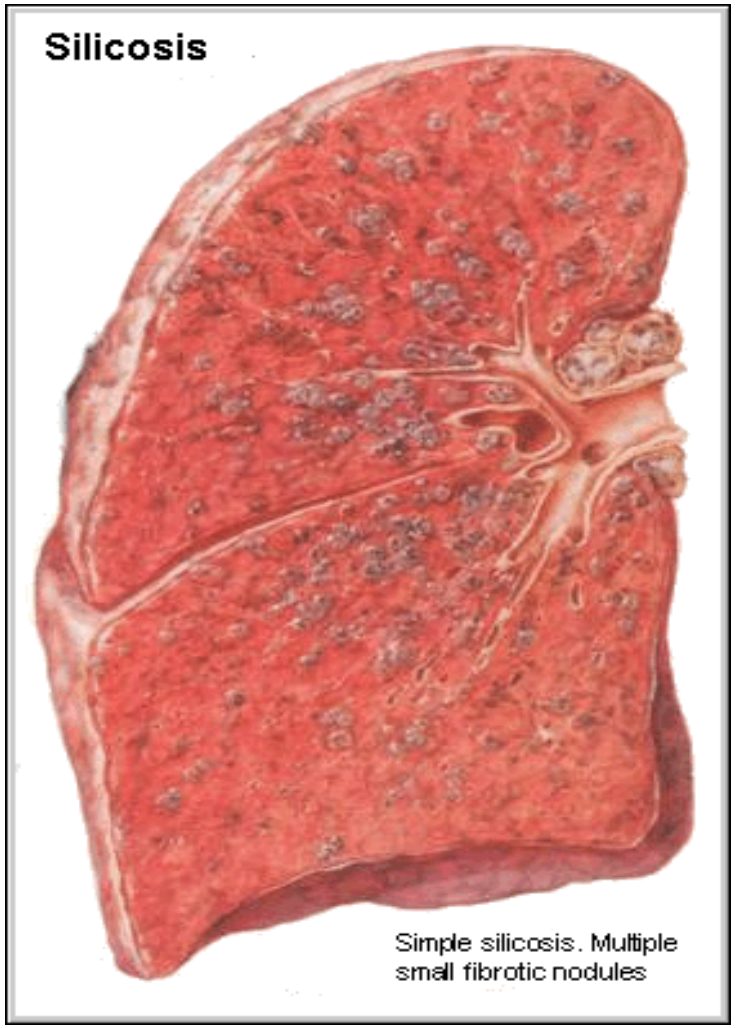
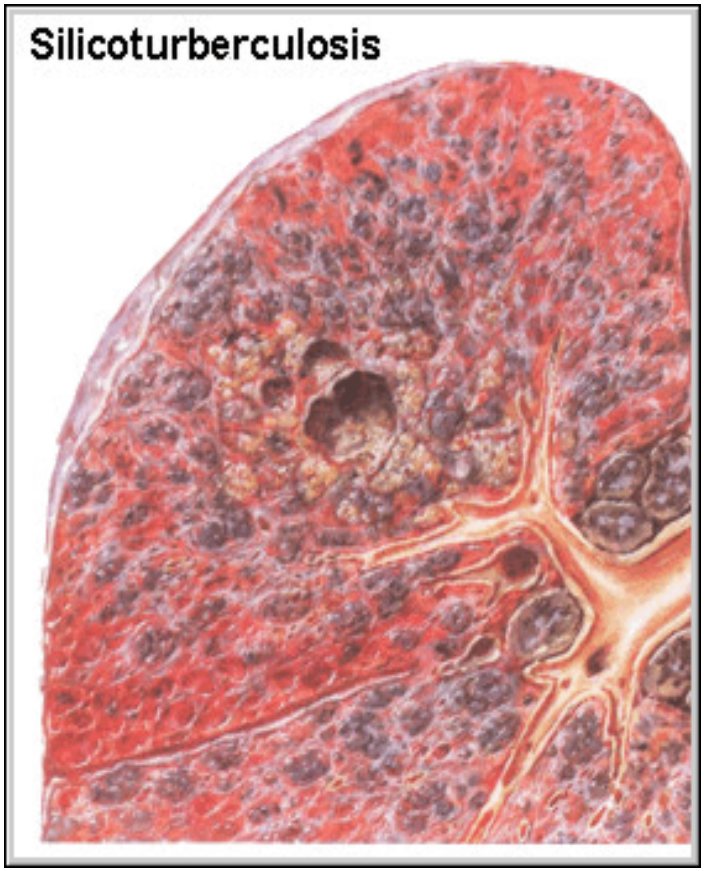
- **Silicosis – nodular fibrosis**





Silica Exposure Limits

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- **OHS Act – Regulations for Hazardous Chemical Substances**

Substance	Occupational Exposure Limit	
	TWA OEL-RL mg/m³	Short Term OEL-RL mg/m³
*Silica, crystalline respirable dust (SiO_2)	0.1	-
Silica, amorphous (SiO_2):		
total inhalable dust	6	-
respirable dust	3	-
Silica, fused respirable dust (SiO_2)	0.1	-

Silica Exposure Limits

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- **OHS Act – Regulations for Hazardous Chemical Substances**
  - *** Exposure Limit in Table 1 of the Regulations – by definition it refers to all forms of crystalline Silica.**
  - **In Table 2 of the Regulations other OELs (i.e. 0.4mg/m^3) for the other polymorphs (Cristobalite and Tridymite) as well as Tripoli are listed, but by default, according to the above, those "outdated" OELs are not applicable.**

Silica Exposure Limits

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- **MHS Act – OH Regulations**

Substance	Occupational Exposure Limit	
	TWA OEL-RL mg/m³	Short Term OEL-RL mg/m³
Diatomaceous earth, natural (SiO_2) [respirable particulate] (68855-54-9)	1.5	-
Silica, amorphous (SiO_2): total inhalable particulate respirable particulate (7631-86-9)	 6 3	 - -
Silica, crystalline [respirable particulate] (SiO_2): Cristobalite (14464-46-1) Quartz (14808-60-7) Tridymite (15468-32-3) Tripoli (1317-95-9)	 0.1 0.1 0.1 0.1	 - - - -
Silica fume [respirable particulate] (SiO_2) (69012-64-2)	2	-
Silica, fused [respirable particulate] (SiO_2) (60676-86-0)	0.1	-

Measurement – Respirable particulates

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- **NIOSH 0600:**
  - Sampler: Cyclone and Membrane filter (Higgins-Dewell (HD) cyclone and 37mm diameter and 5-µm pore size PVC membrane filter)

Measurement – Respirable particulates

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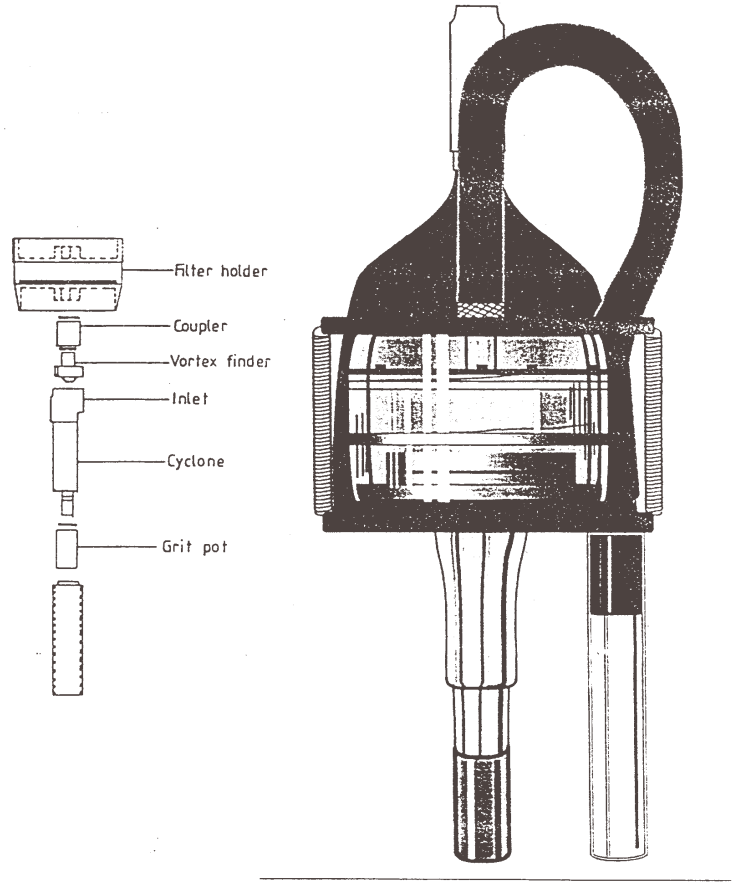
Sampling:

- This cassette incorporates a cyclone which separates respirable dust form the rest.
- Through its design respirable size fraction particles are allowed through onto the filter paper and the larger ones drop into the grit pot.
- To collect a respirable dust sample the sampling pump should run at 2.2 or 1.9 ℓ/minute, depending on.....



CYCLONE ASSEMBLY FOR RESPIRABLE DUST/FUME SAMPLING

Measurement – Respirable particulates

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Sampling – flow rates (using the HD Cyclone):

- **OHS Act – 1.9ℓ/min to collect respirable dust according to the Johannesburg curve:**

  (i) 100 % particles of 1 µm aerodynamic diameter,

  (ii) 50 % particles of 5 µm aerodynamic diameter,

  (iii) 20 % particles of 6 µm aerodynamic diameter,

  (iv) 0 % of particles of 7 µm aerodynamic diameter and larger to pass through the size selector.

Measurement – Respirable particulates

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Sampling – flow rates (using the HD Cyclone):

- **MHS Act – 2.2ℓ/min to collect respirable dust according to the ISO (ACGIH, OHSA) curve:**

  (i) 100 % particles of 0 µm aerodynamic diameter,

  (ii) 50 % particles of 4 µm aerodynamic diameter,

  (iii) 30 % particles of 5 µm aerodynamic diameter,

  (iv) 1 % of particles of 10 µm aerodynamic diameter and larger to pass through the size selector.

Analyses

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- **NIOSH Method 7500 -** SILICA, CRYSTALLINE, By XRD (X- RAY POWDER DIFFRACTION). Accuracy = ± 18%
- **NIOSH Method 7601 -** SILICA, CRYSTALLINE by VIS (VISIBLE ABSORPTION SPECTROPHOTOMETRY). Accuracy = Not Determined
- **NIOSH Method 7602 -** SILICA, CRYSTALLINE by IR (INFRARED ABSORPTION SPECTROPHOTOMETRY). Accuracy = Not Determined
- **On-Filter X-Ray Diffraction.**

But

- **Never, ever rely on "SiO_2" results derived from ICP analysis**

Control of Exposure

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- Depending on concentration
- As for any other airborne particulate
- Dependant on circumstances
- Hierarchy of control

General

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- **General Discussion and Questions**

Thank You

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