Respirable Crystalline Silica Sampling and Laboratory Analysis

March 22, 2018

Keith P. Rickabaugh, CIH

RJ LEE GROUP
DELIVERING SCIENTIFIC RESOLUTION

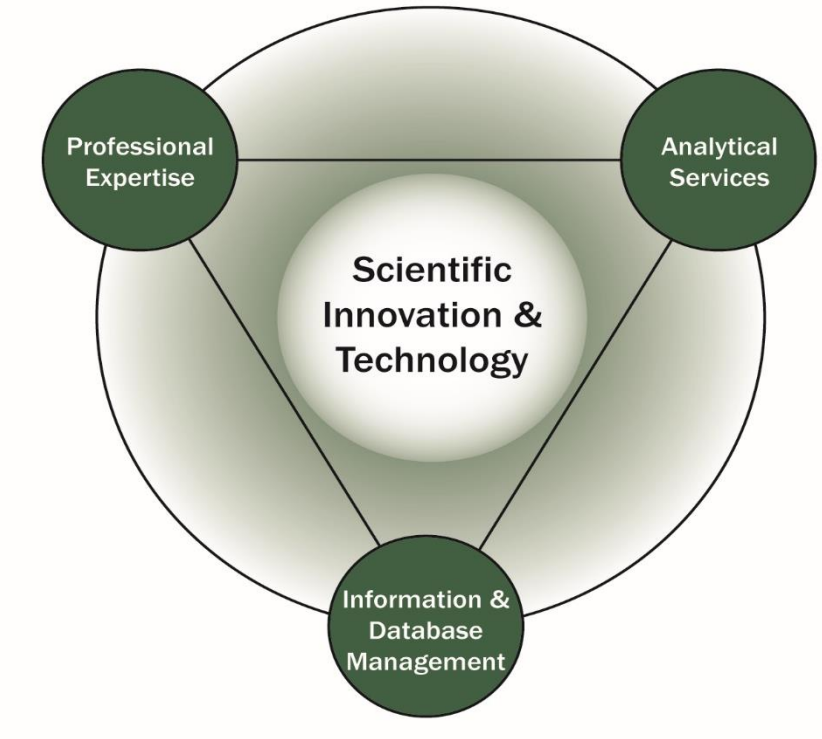
Meeting Agenda

11:00-11:15	**Registration**
11:15 - 12:00	**RCS Sampling and Laboratory Analysis – Keith Rickabaugh**
12:00-12:30	**Lunch meeting and discussion**
12:30-1:15	**“The Challenges of Sampling for Silica for Half a Century / Lessons Learned” - Bob Wheeler**
1:15-2:00	**RCS OSHA Regulations Overview - Del Kubeldis**
2:00-2:45	**Field Perspectives, IH Monitoring for RCS - Thad Pajak**
2:45-3:30	**Laboratory Tour – Resp. Crystalline Silica by XRD**

About RJ Lee Group

Core Competencies

Professional Expertise
Industrial Hygiene
Nanotechnology
Criminal Forensics
Litigation Support
Environmental Forensics
Materials Characterization
Construction Materials



Analytical Services
Microscopy
- Optical
- Scanning Electron
- High Resolution SEM
- Transmission Electron

ESCA/XPS
X-ray Diffraction
Chemical Analysis

Information & Software Services
Laboratory Information Management Systems
Data Management & Integration Solutions
Application Development

Our People

RJ Lee Group employs over 200 people with backgrounds in various disciplines

- Biological Sciences
- Chemistry
- Chemical Engineering
- Computer Science
- Electrical Engineering
- Environmental Science
- Geology
- Industrial Hygiene
- Materials Science
- Mathematics
- Mechanical Engineering
- Metallurgy
- Meteorology
- Mineral Processing
- Mineralogy
- Physics

Over 1,000 technical papers published and presented.

Memberships in 30 professional societies.

Laboratory Analysis Capabilities

- Microscopy
  - Optical microscopes
  - Scanning electron microscopes
  - Transmission electron microscopes
  - High resolution electron microscopes
- Surface Analysis: ESCA/XPS
- X-ray Diffraction (XRD)
- X-ray Fluorescence (XRF)
- Fourier Transform Infrared Spectroscopy(FTIR)
- Raman Spectroscopy
- Analytical Chemistry
  - ICP-AES and ICP-MS
  - AA and IC
  - GC-MS, GC-FID, GC-ECD
  - DSC / TGA

Exposure to Crystalline Silica

- Rock – an aggregate of minerals
  - Igneous – granite, other felsic igneous rocks
  - Sedimentary – sandstone, shale, carbonates
  - Metamorphic – schist, gneiss, quartzite, etc.
- Many Industries Involved
  - Mining and Processing
  - Construction
  - Agriculture
- Potential Risk for Delayed Health Effects (chronic):
  - Silicosis
  - Lung cancer
  - Chronic obstructive pulmonary disease (COPD)
  - Kidney disease, TB, auto immune disease (arthritis)?

Potential Work Activities of Concern

- Oil and Gas Industry (e.g., Frac Sand)
- Stone Cutting and Polishing
- Foundry Operations
- Sand Blasting
- Manufacturing (e.g., Glass and Ceramics)
- Concrete, Masonry and other Construction Materials
- Abrasives
- Building Demolition / Renovation
- Mining (various)
- Materials Handling / Packaging
- Agriculture

Current OSHA Standard – General Industry

$$\text{OSHA PEL}^* = \frac{10}{\%\ SiO_2 + 2}\ (mg/m^3)$$

- Ref. 29 CFR 1910.1000
- *The formula shown is for quartz.
- Tridymite and Cristobalite are ½ this value.
- ACGIH TLV = 0.025 mg/m^3

OSHA Rationale for Revised Standard

- 1971 Standard is Outdated
- Suggests that current standard is not adequate
  - IARC, NIOSH, and National Tox. Program
- Old Standard Difficult to Understand by Many
  - Weighted Dust Formula (General Industry)
  - Construction and Shipyards Different
- Consistent Level of Protection Needed

Ongoing Controversy

- Scientific certainty of risk analysis for PEL
  - Foundation of data and methods used
  - Possible threshold effect for cancer risk
- Better enforcement of prior standard may be adequate?
- Industry is already addressing issues
- Economic analysis questions
- Technical feasibility issues
  - Engineering controls and work practices
  - Sampling/Measurement for low levels of exposure

Record Keeping – General Industry

Exposure Monitoring – Air Sampling

- Sample dates and tasks
- Sampling and analytical method used
- Number, duration and results for samples
- Laboratory identity
- PPE utilized during sampling
- Social Security Numbers for employees covered

Objective Data

- Materials in question
- Data sources
- Testing protocols / results
- Descriptions of processes and tasks
- Other relevant data

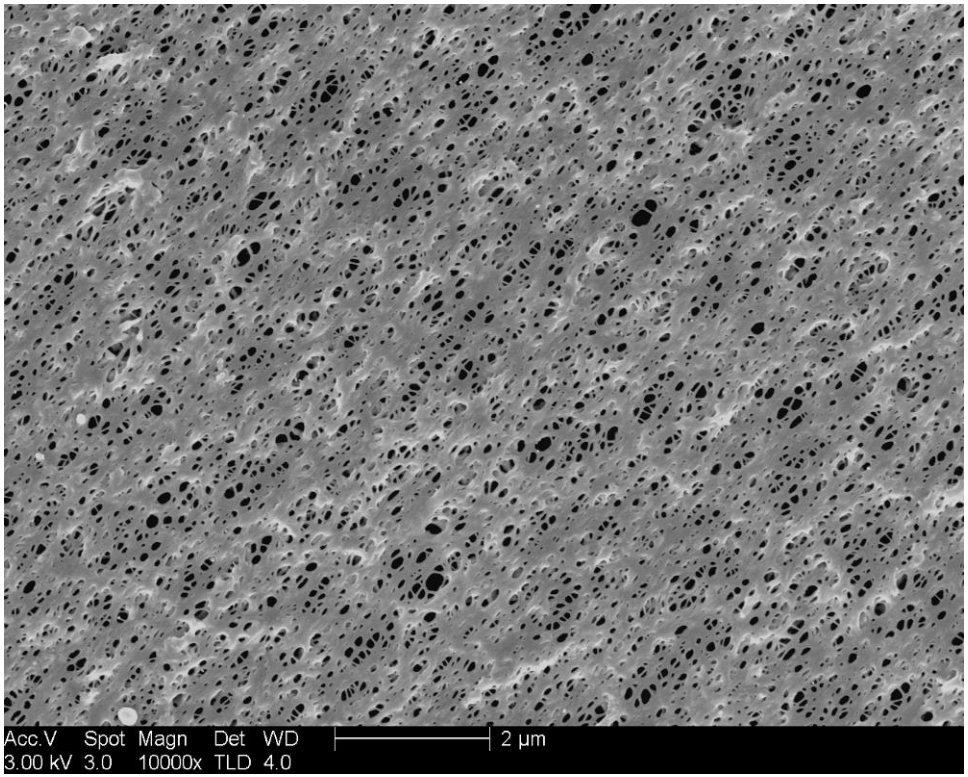
Exposure Monitoring
Sampling and Lab Methods

Methods (Crystalline Silica on Filters)

- MSHA – P7 (FTIR) – coal mines
- MSHA – P2 method (XRD) – metal/non metal mines
- NIOSH – 7500 (XRD)
- ~~NIOSH – 7601 (Chemical-VIS)~~
- NIOSH – 7602 (IR-KBr pellet)
- NIOSH – 7603 (IR-redeposition)
- OSHA – ID #142 (XRD)

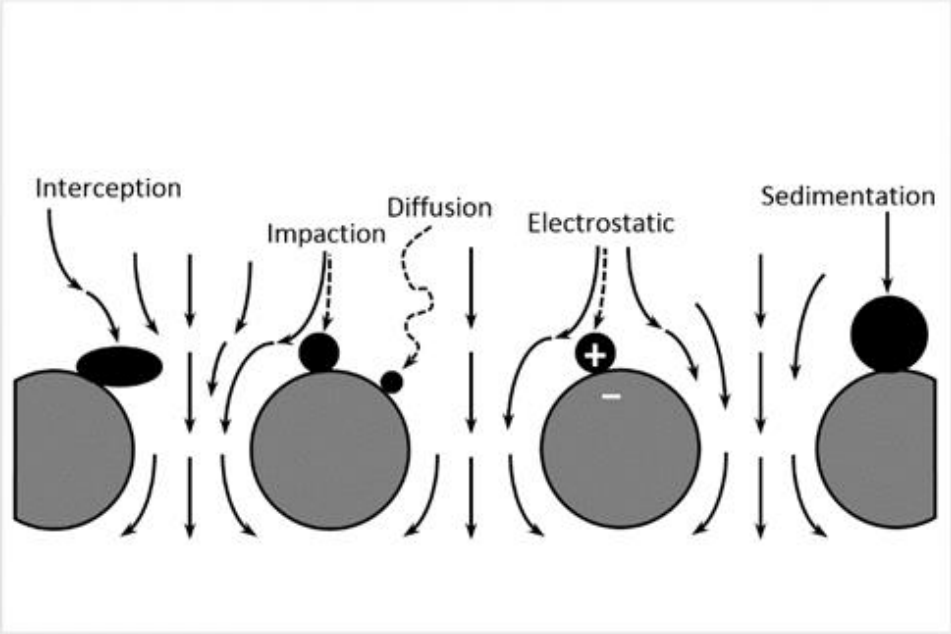
Polyvinyl Chloride (PVC) Filters

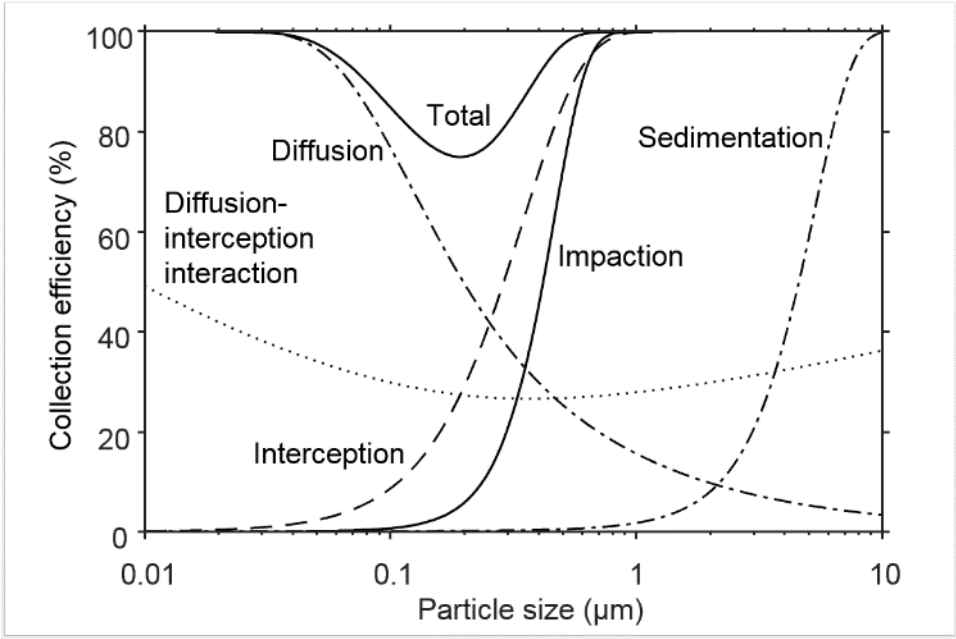
- Suitable for multiple NIOSH/OSHA/ASTM air sampling methods
  - Silica
  - Metals
  - Dust (silica-free, low ash)
- Hydrophobic - low tare weight and moisture pickup for gravimetric stability
- Non-oxidizing surface



Secondary electron image of a PVC filter

PVC Air Filters
Particle Collection Efficiency





5 μm Pore Size PVC filters > 98% collection efficiency at 2.5 lpm.

Images Credit: NIOSH Manual of Analytical Methods – 5th Edition, Chapter FP

Useful Reference – Testing Air Filters

Published in final edited form as:

Aerosol Sci Technol. 2016 January ; 50(1): 76–87.

Air sampling filtration media: Collection efficiency for respirable size-selective sampling

Jhy-Charm Soo[a], **Keenan Monaghan**[a], **Taekhee Lee**[a], **Mike Kashon**[b], and **Martin Harper**[a]

[a]Health Effects Laboratory Division, Exposure Assessment Branch, National Institute for Occupational Safety and Health, Morgantown, West Virginia, USA

[b]Health Effects Laboratory Division, Biostatistics and Epidemiology Branch, National Institute for Occupational Safety and Health, Morgantown, West Virginia, USA

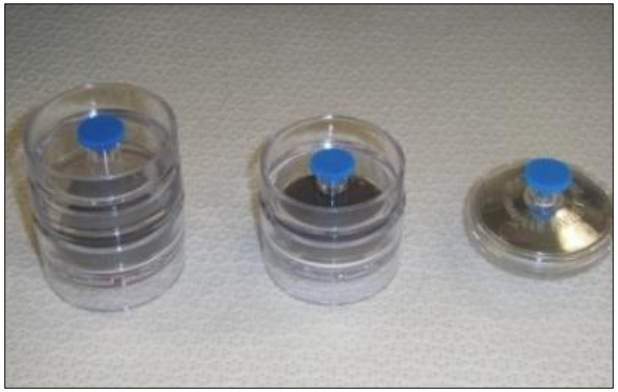
Sample Collection

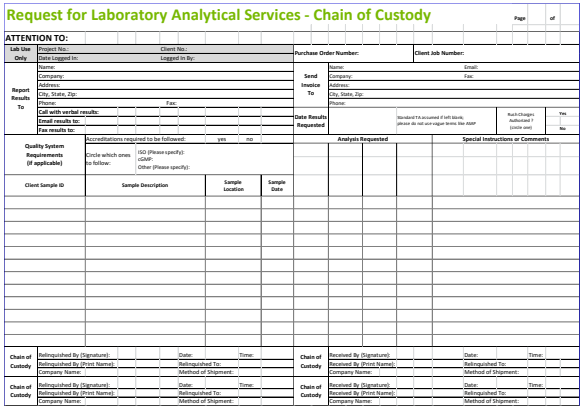
XYZ Company Sample Collection Record

Sample Date	Sample No.	Sample Description	Media	Pump No.	Pre-Flow Rate (L/min)	Start Time	Post-Flow Rate (L/min)	Stop Time	Avg. Flow Rate	Total Time (min)	Volume (L)	Analysis
		Personal - Total Dust	PVC (5.0)						0.0	0	0.0	NIOSH 0500
		Personal - Resp / Silica	PVC (5.0)						0.0	0	0.0	NIOSH 0600/7500
		Area 1 - Total Dust	PVC (5.0)						0.0	0	0.0	NIOSH 0500
		Area 1 - Resp / Silica	PVC (5.0)						0.0	0	0.0	NIOSH 0600/7500
		Area 2 - Total Dust	PVC (5.0)						0.0	0	0.0	NIOSH 0500
		Area 2 - Resp / Silica	PVC (5.0)						0.0	0	0.0	NIOSH 0600/7500
		PDR - Resp / Silica	PVC (5.0)						0.0	0	0.0	NIOSH 0600/7500
		Field Blank	PVC (5.0)						0.0	0	0.0	NIOSH 0500
		Field Blank	PVC (5.0)						0.0	0	0.0	NIOSH 0600/7500

Chain of Custody

Relinquished by:		Date/Time		
Method of Shipment: Hand delivered				
Received by:		Date/Time		
Sample Condition Upon Receipt:	Acceptable		Other (explain on reverse)	





What is a Respirable Particle?

- < 10 microns (aerodynamic mass diameter)
- Inhaled particles can reach deep regions of lung (Alveoli)

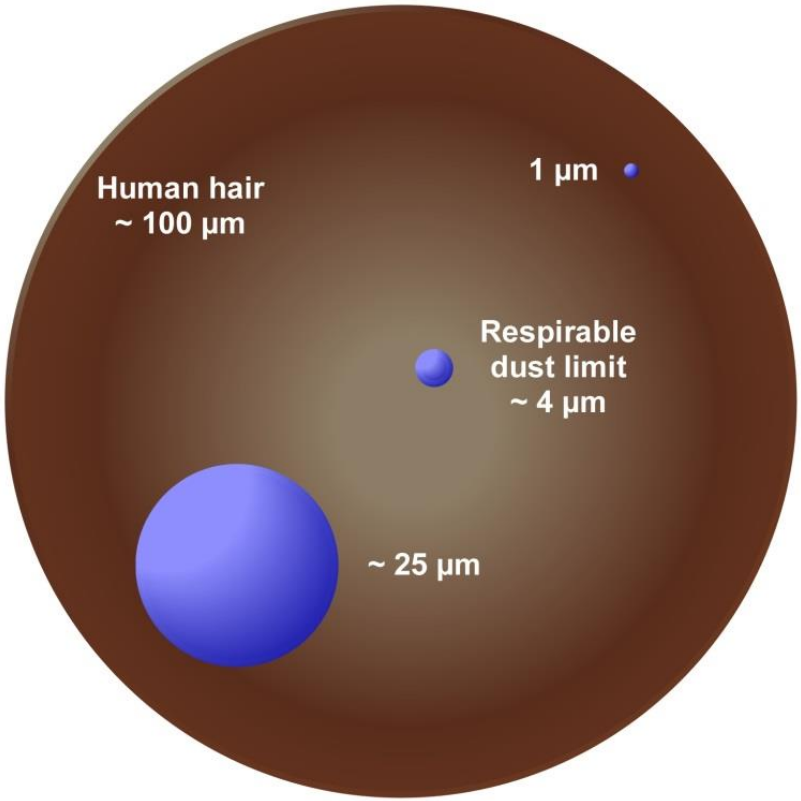
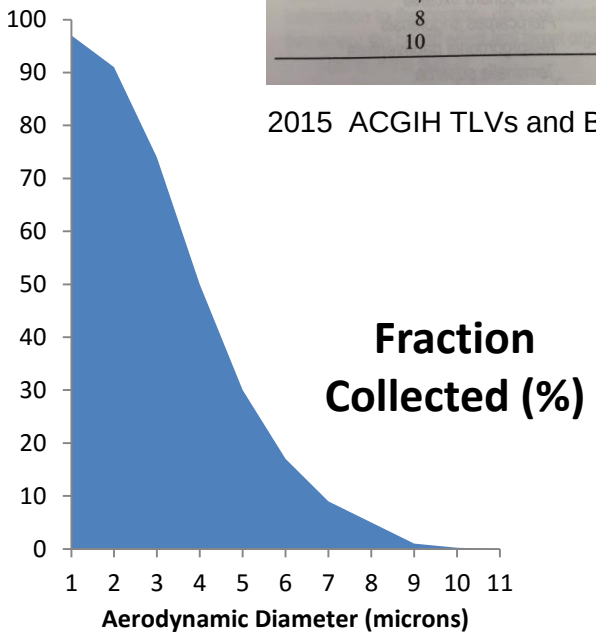


TABLE 3. Respirable Fraction

Particle Aerodynamic Diameter (µm)	Respirable Particulate Matter (RPM) Fraction Collected (%)
0	100
1	97
2	91
3	74
4	50
5	30
6	17
7	9
8	5
10	1

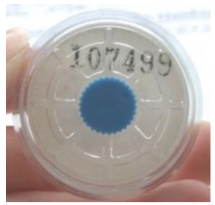
2015 ACGIH TLVs and BEIs Appendix C

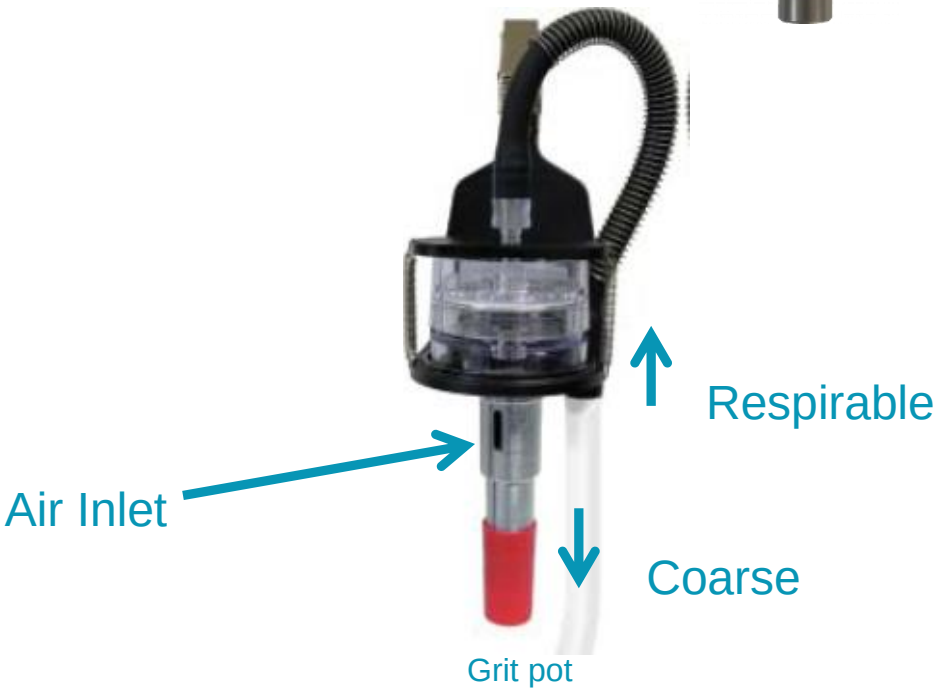


Size Selective Sampling – Cyclones

Cyclone	Flow Rate
10-mm nylon cyclone (Dorr Oliver)	1.7 L/min
Higgins-Dewell (HD) cyclone	2.2 L/min
SKC Aluminum cyclone	2.5 L/min
BGI GK 2.69 cyclone	4.2 L/min

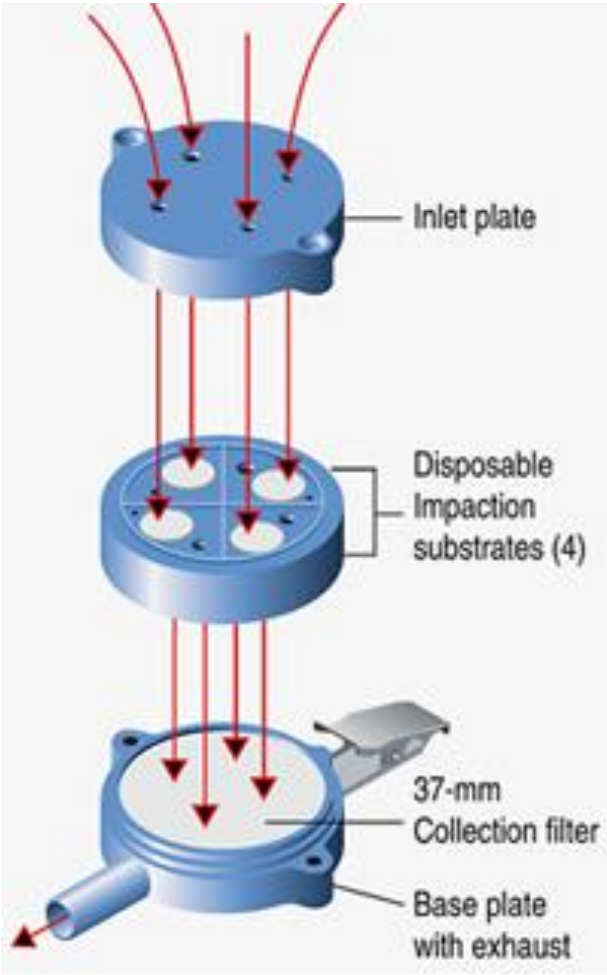
- Ensure the cassette is loaded into the cyclone properly
- Do not invert sampler assembly while using the cyclone



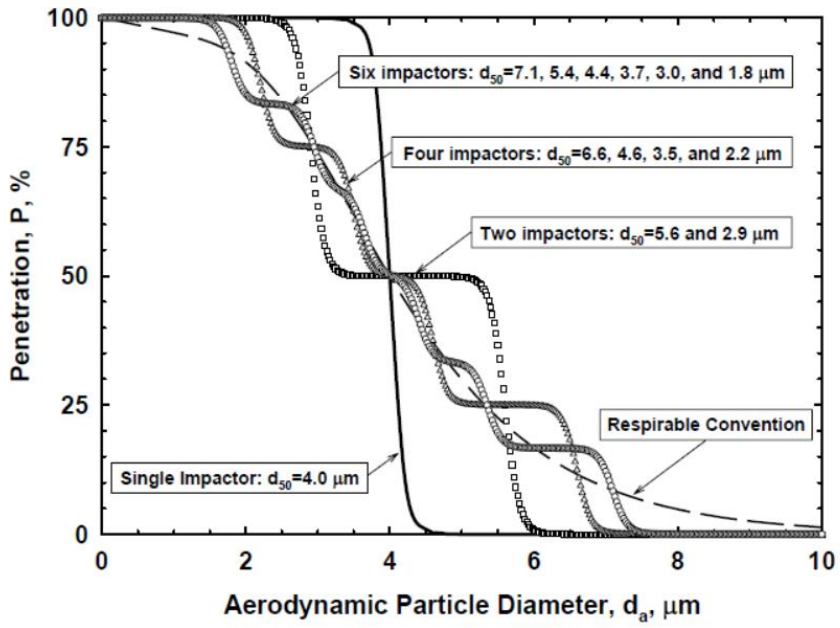


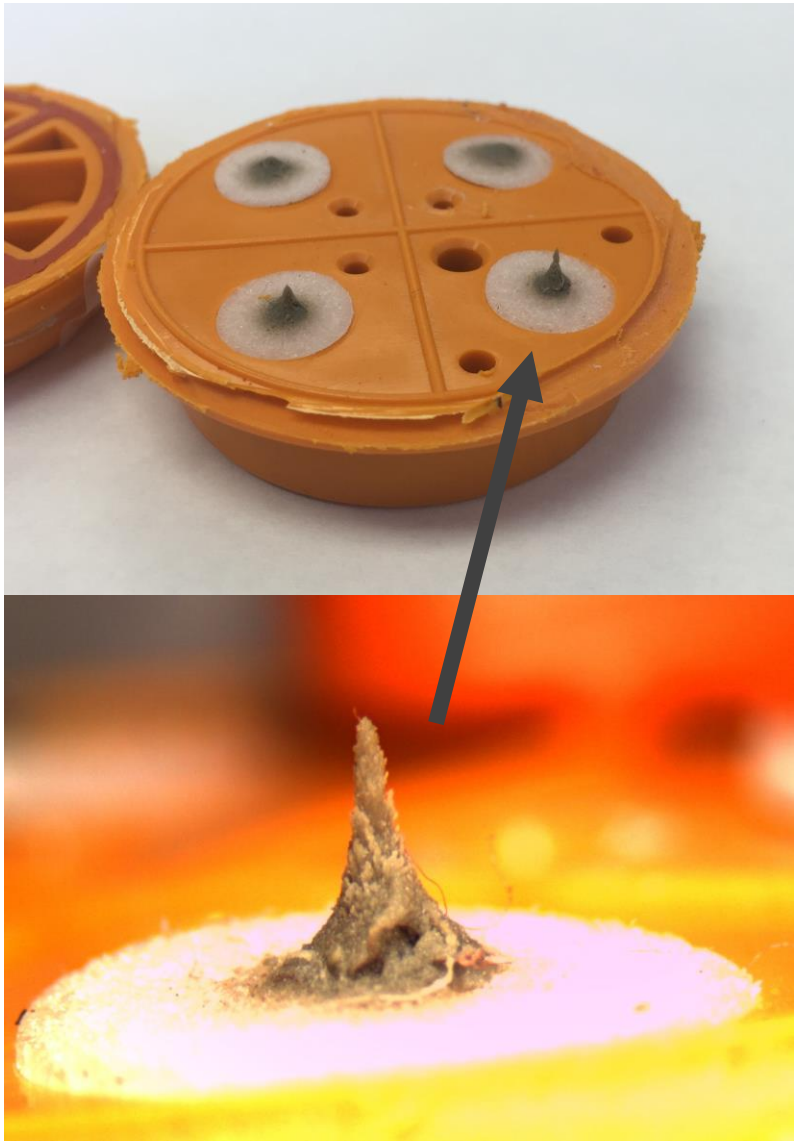
SKC Personal Parallel Impactor (PPI)

- Easy-to-use and disposable
- 2, 4 and 8 liters per minute options
- Lightweight for worker comfort
- Calibration cap available
- Less training required
- No inversion issues or cleaning
- ISO 7708/CEN respirable convention



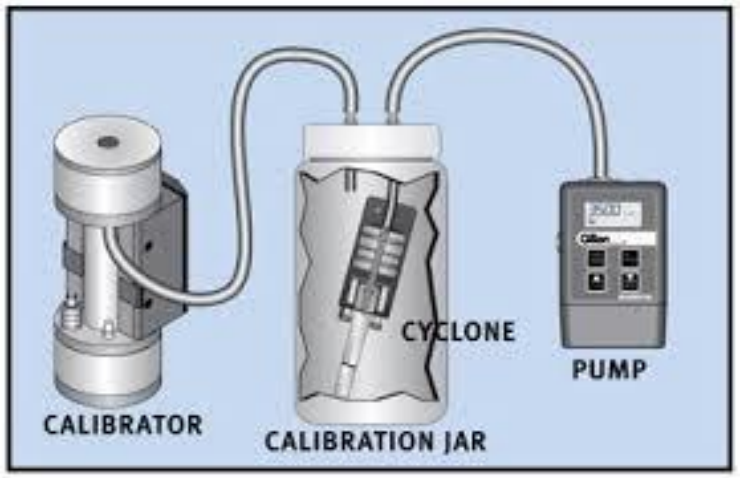
SKC Personal Parallel Impactor (PPI)



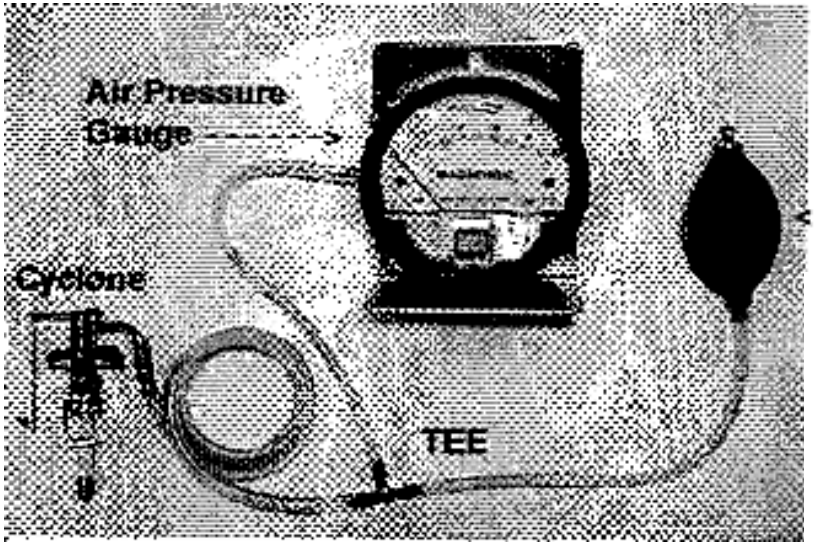


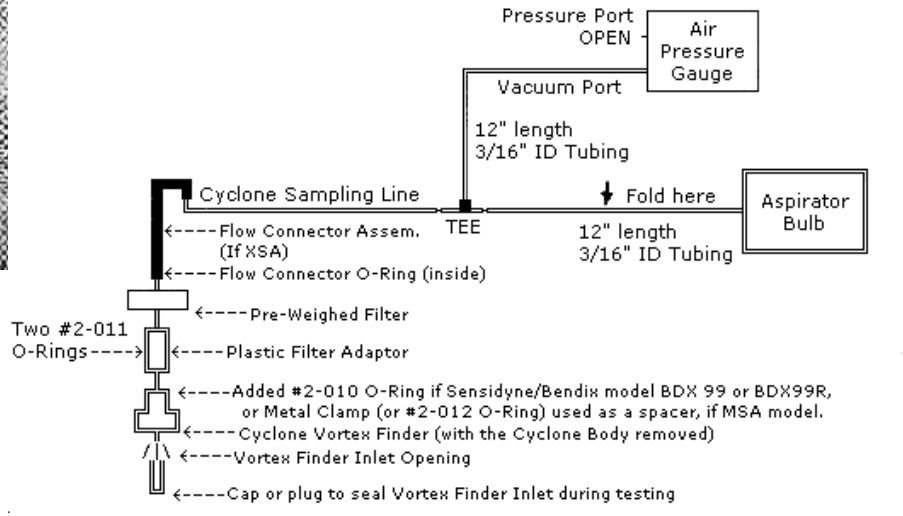
Sampler Calibration

- Calibrate flow rate to primary standard
- Include entire sampling train
- Bell jar vs. direct flow check
- Check flow rate before and after sampling



OSHA Leak Testing Procedure





- Must have less than 25% loss in partial pressure after 30 seconds.

Reference: OSHA Directorate of Technical Support and Emergency Management (DTSEM)/Cyclone Leak Test Procedure

OSHA RCS Standard(s) – Appendix A (Laboratory) LOQ and Air Sampling Volumes

"6.3 Optimizes methods and instruments to obtain a quantitative limit of detection that represents a value ***no higher than 25 percent of the PEL based on sample air volume****."*

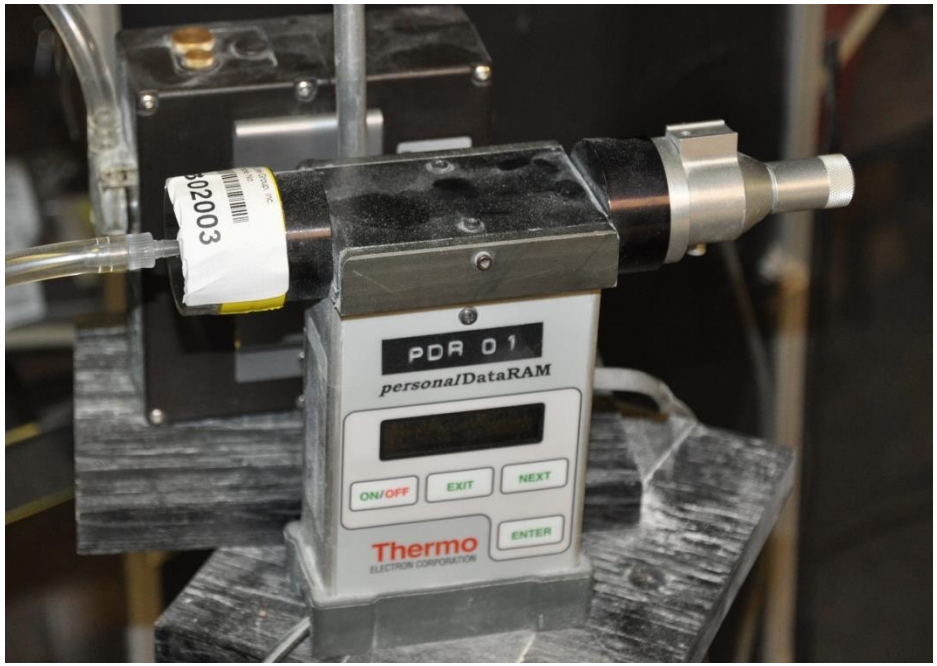
Lab LOQ µg/filter	Air Volume (liters)*	Min. Sampling Times (hours) Recommended			
		Dorr-Oliver (1.7 lpm)	PPI - Tan (2.0 lpm)	SKC Aluminum (2.5 lpm)	PPI - Orange (4.0 lpm)
20	1600	15.7	13.3	10.7	6.7
10	800	7.8	6.7	5.3	3.3
5	400	3.9	3.3	2.7	1.7
2.5	200	2.0	1.7	1.3	0.8

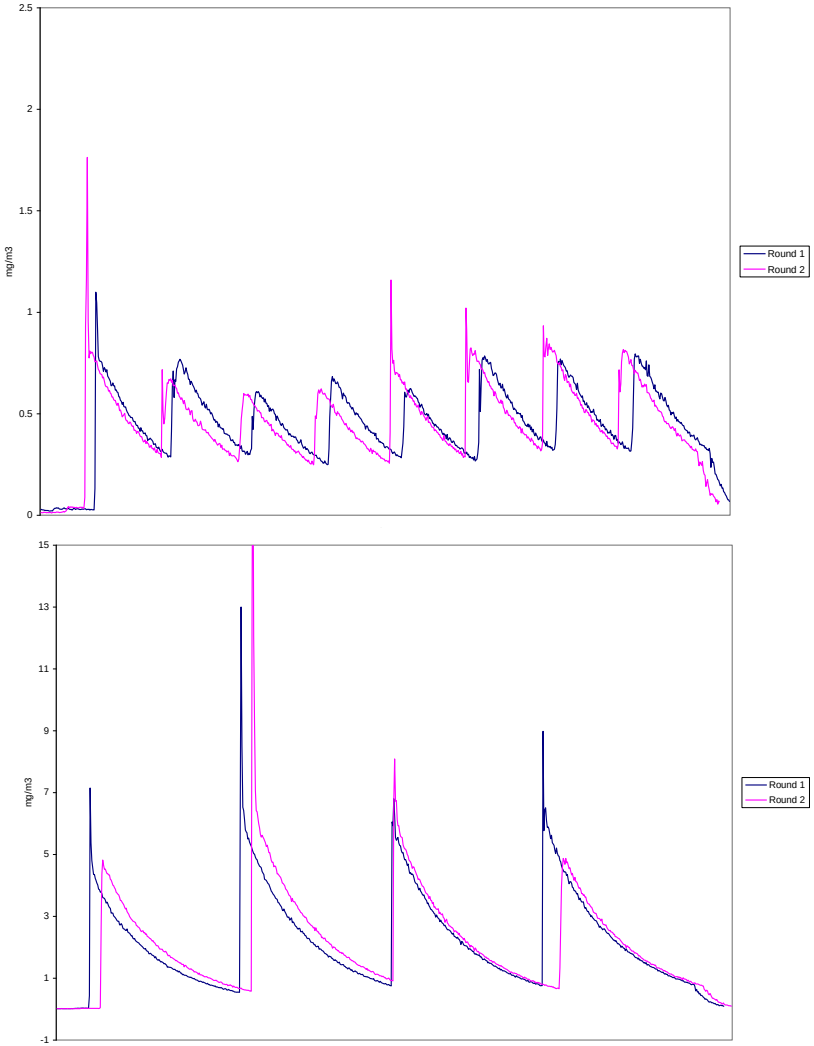
** Based on amount to meet 25% of PEL*

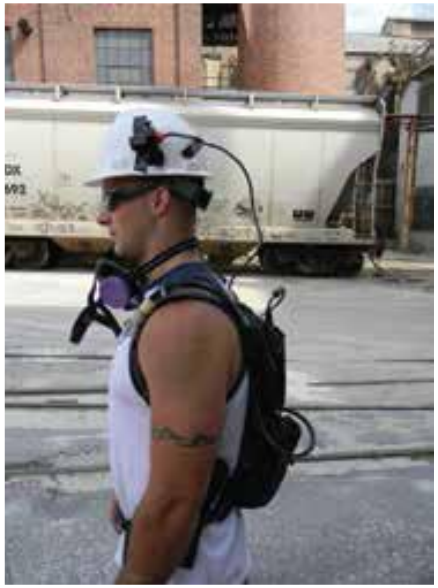
Exposure Monitoring Tips

- Inspect and Test Equipment
  - Cassettes for cracks / leaks
  - Integrity of tubing
  - O-rings and seals
  - Clean cyclone and grit pot
- Orientation of Sample Inlet and Cyclone
- Maximize Sampling Air Volume
- Know Where your Sampler has Been
- Augment with Direct-reading Instruments
- Avoid Sampler Contact with Settled Dust
- Referee Potential Interferences

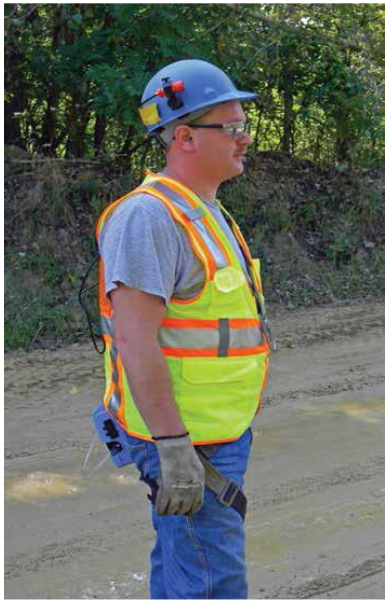
Direct-reading Instrument Example
Circular Saw vs. Rotary Saw

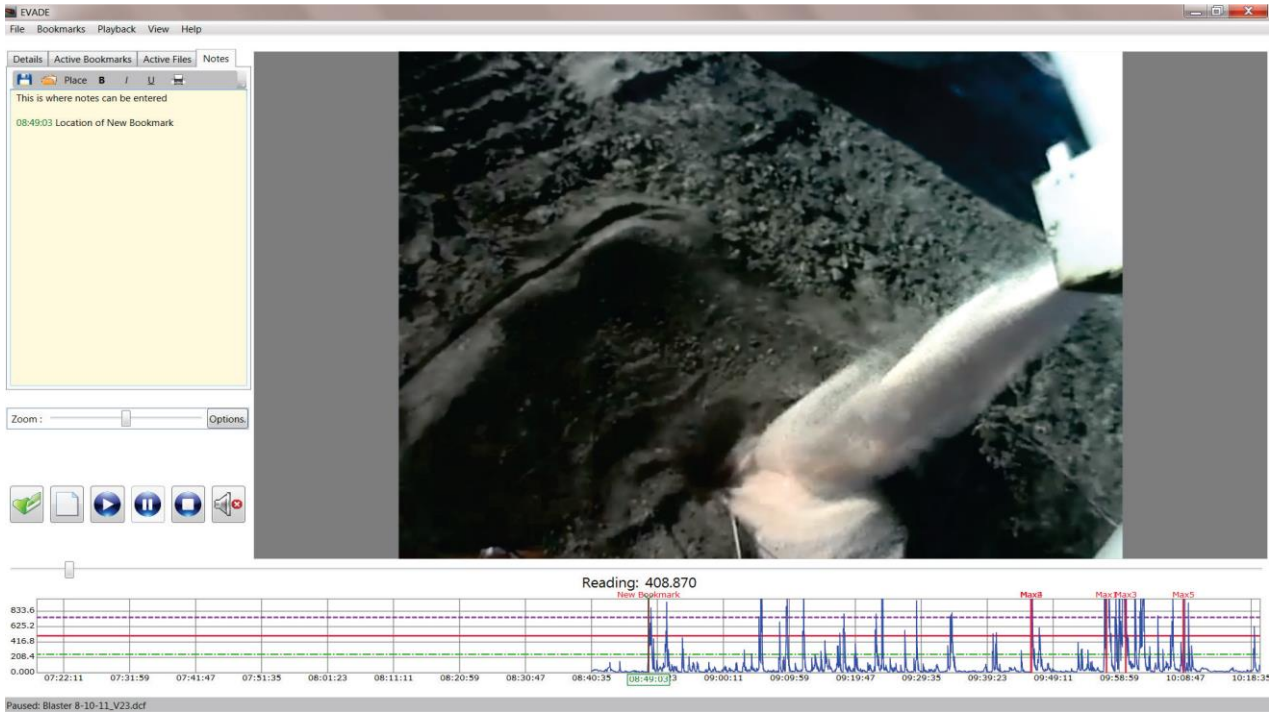






NIOSH EVADE Software





NIOSH 7500 (and 0600) Laboratory Analysis

Follow a Sample through the Laboratory

Why use X-ray Diffraction (XRD)?

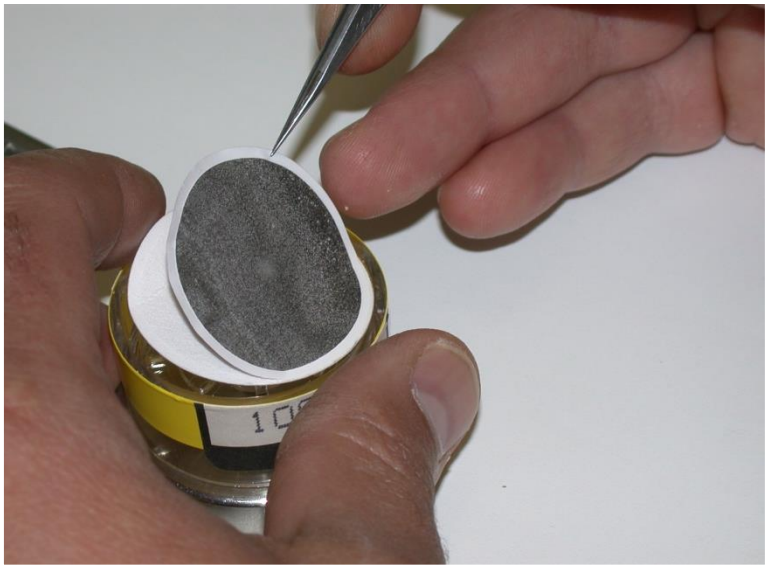
- Used to Evaluate Crystalline Materials
- NIOSH 7500, Crystalline Silica by XRD
- OSHA Regulates Respirable Crystalline Silica
  - three regulated crystalline silica minerals
  - quartz, cristobalite, and tridymite
- Also used to Identify Specific Compounds
  - CaO, $CaCO_3$, $Ca(OH)_2$
  - CaS, $CaSO_4$, $CaSO_4 \cdot 2H_2O$, $CaSO_4 \cdot 0.5H_2O$
  - FeO, Fe_2O_3, Fe_3O_4, $FeO(OH)$

Cassette Assembly

- Filters Used
  - 5 µm pore size
  - 37 mm diameter
  - Polyvinyl chloride (PVC)
- Pre-weights
  - Weighed in sets of 10
  - Every 10th weight is re-weighed to ensure that the balance did not drift during weighing of the set

Sample Preparation

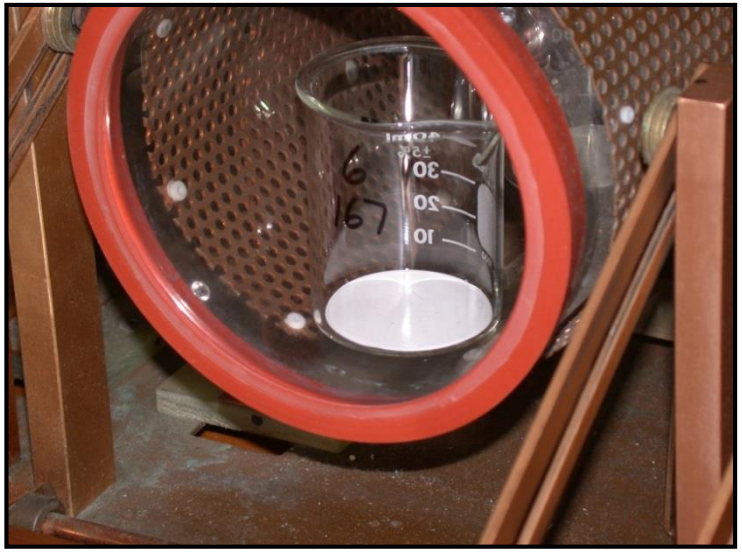
- Samples received
- Dried in a desiccator
- Cassettes carefully opened to remove filters
- Filters post-weighed
- Total respirable dust mass calculated



‘Gravimetric Analysis’
NIOSH 0500
NIOSH 0600

Sample Preparation

- NIOSH 7500 Options
  - Low temperature plasma ashing (beaker)
    - 1 hour
  - Muffle furnace ashing (crucible)
    - 2 hour @ 600°C
  - Filter dissolution
    - Tetrahydrofuran (THF)



Sample Preparation

- 15 mL of 2-Proponal is added to each beaker
- Cover and sonicate
- Obtain a silver membrane filter
  - 25 mm
  - 0.45 µm
- Attach funnel

Sample Preparation

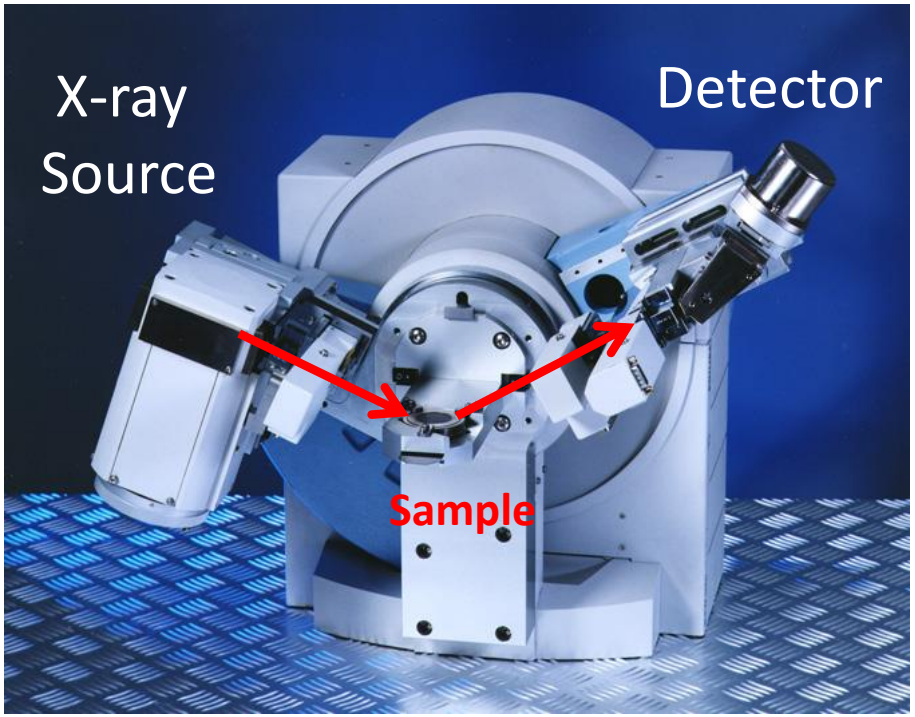
- Pour suspension into the funnel
- Rinse walls of beaker
- Apply vacuum
- Remove the silver filter with the sample deposited on it

Sample Preparation

- Mount into XRD holder
- Place in orderly fashion
- Ready for analysis

X-Ray Diffractometer

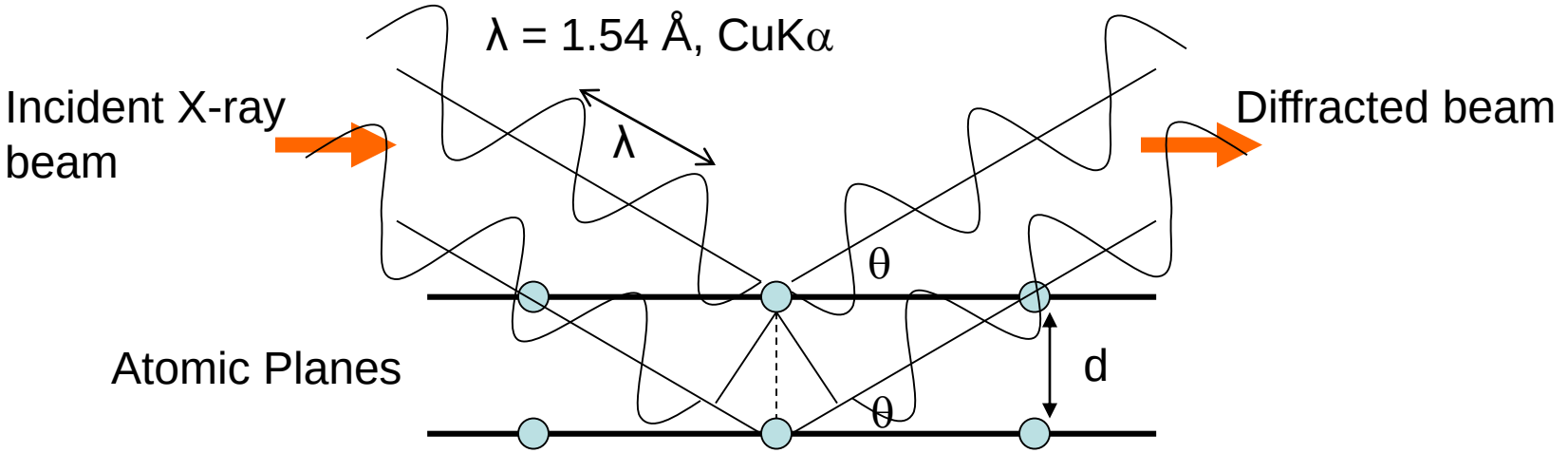
PANalytical Cubix^3 Diffractometer



Goniometer

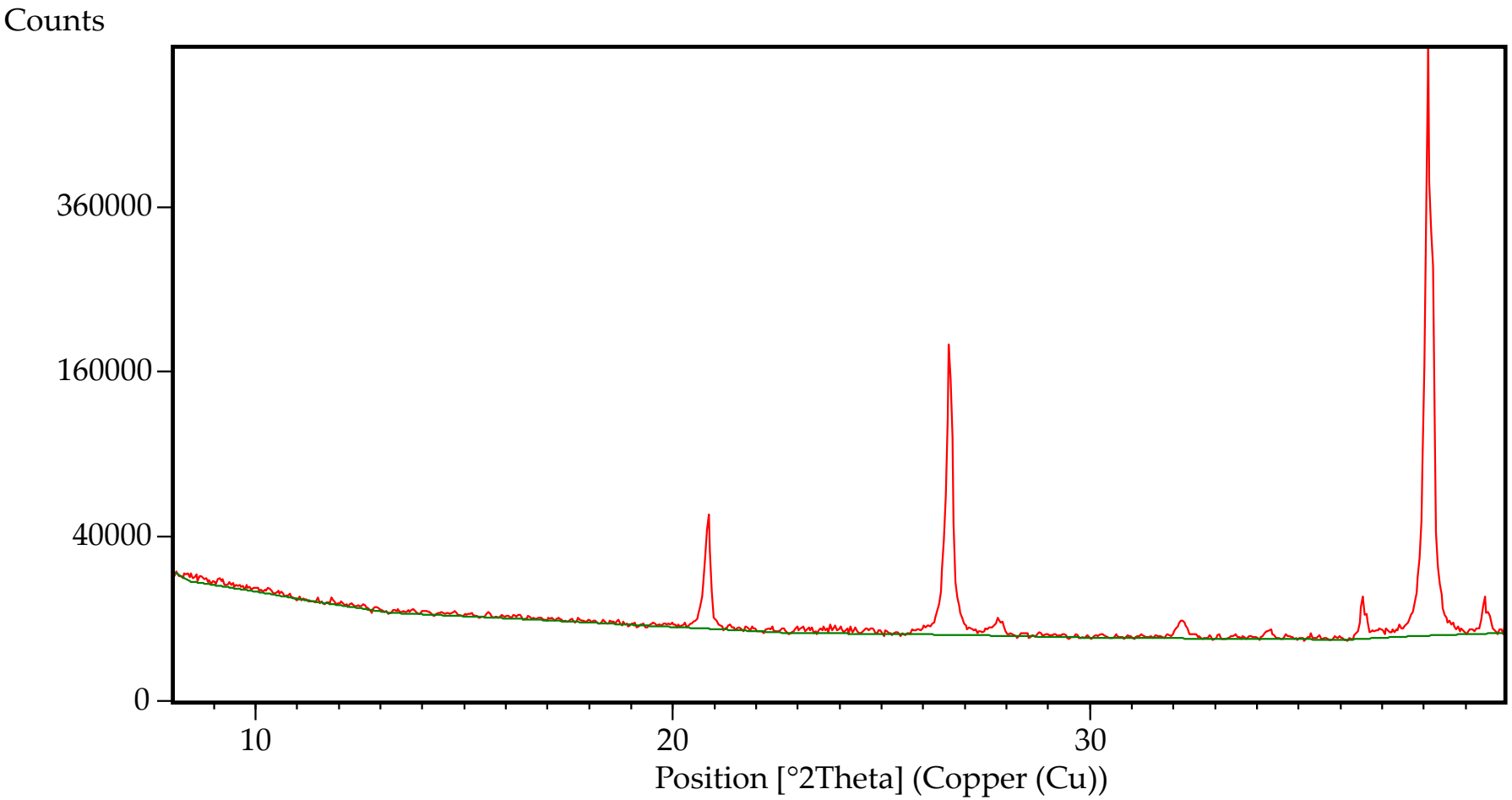
XRD Basics

nλ=2dsinΘ

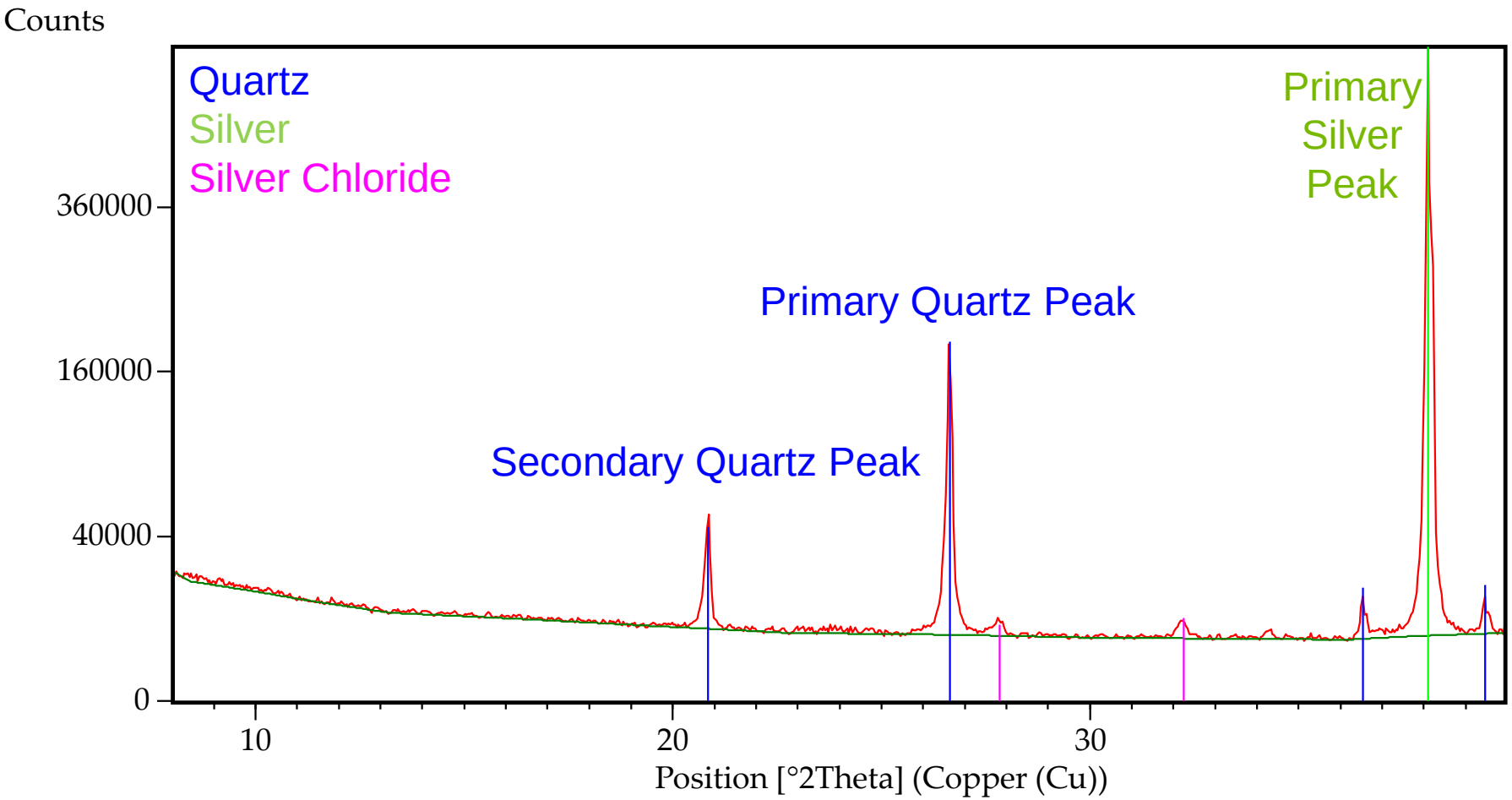


- Bombardment of X-rays results in scattering of the X-rays off of atomic planes
- X-Ray diffraction produces patterns that are indicative of the atomic planes in a material, which serve as a fingerprint for individual minerals

XRD Data


Counts
360000
160000
40000
0
10
20
30
Position [°2Theta] (Copper (Cu))

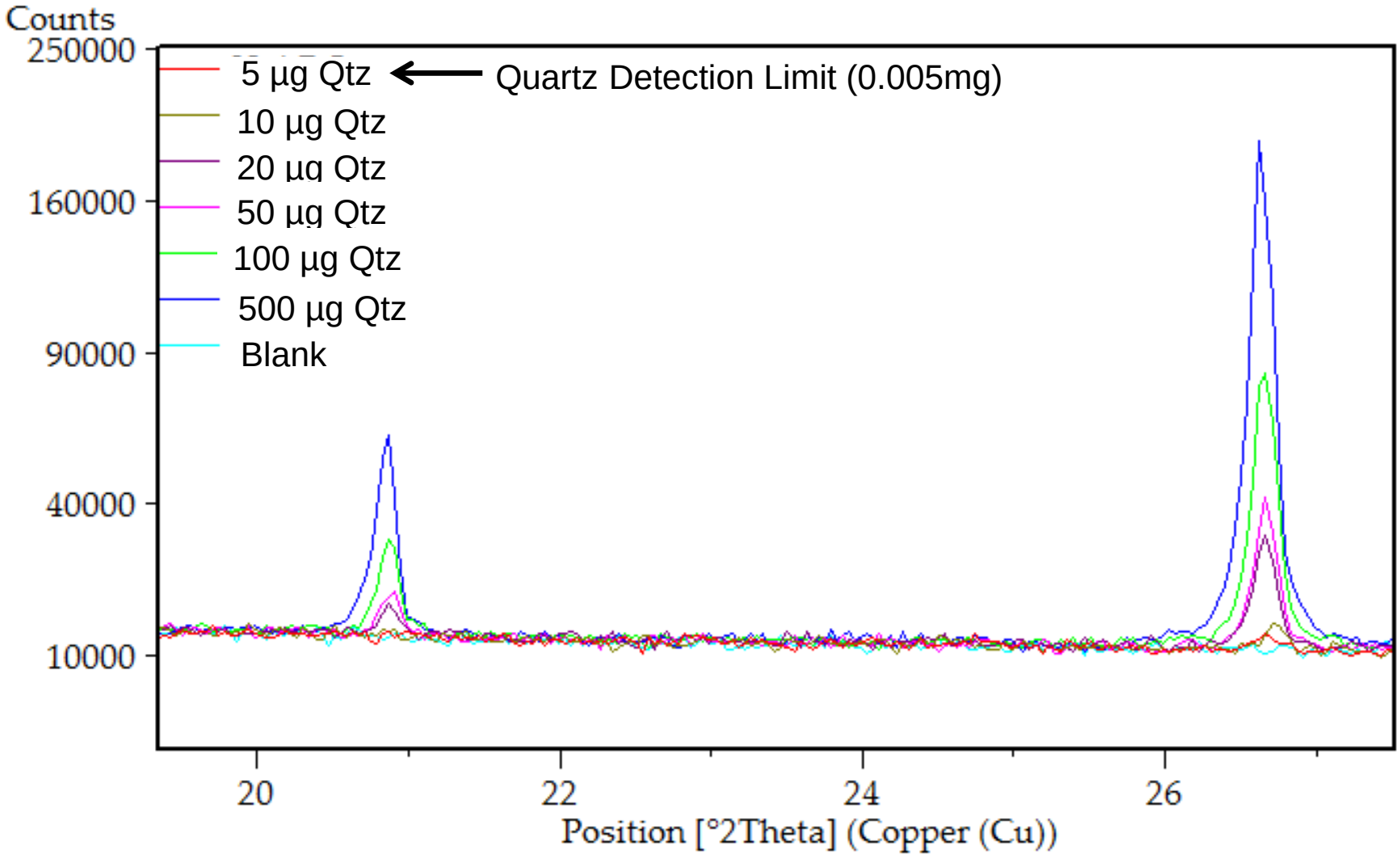
XRD Data


Counts
Quartz
Silver
Silver Chloride
Primary
Silver
Peak
Primary Quartz Peak
Secondary Quartz Peak
360000
160000
40000
0
10
20
30
Position [°2Theta] (Copper (Cu))

NIOSH 7500 - External Standard Method

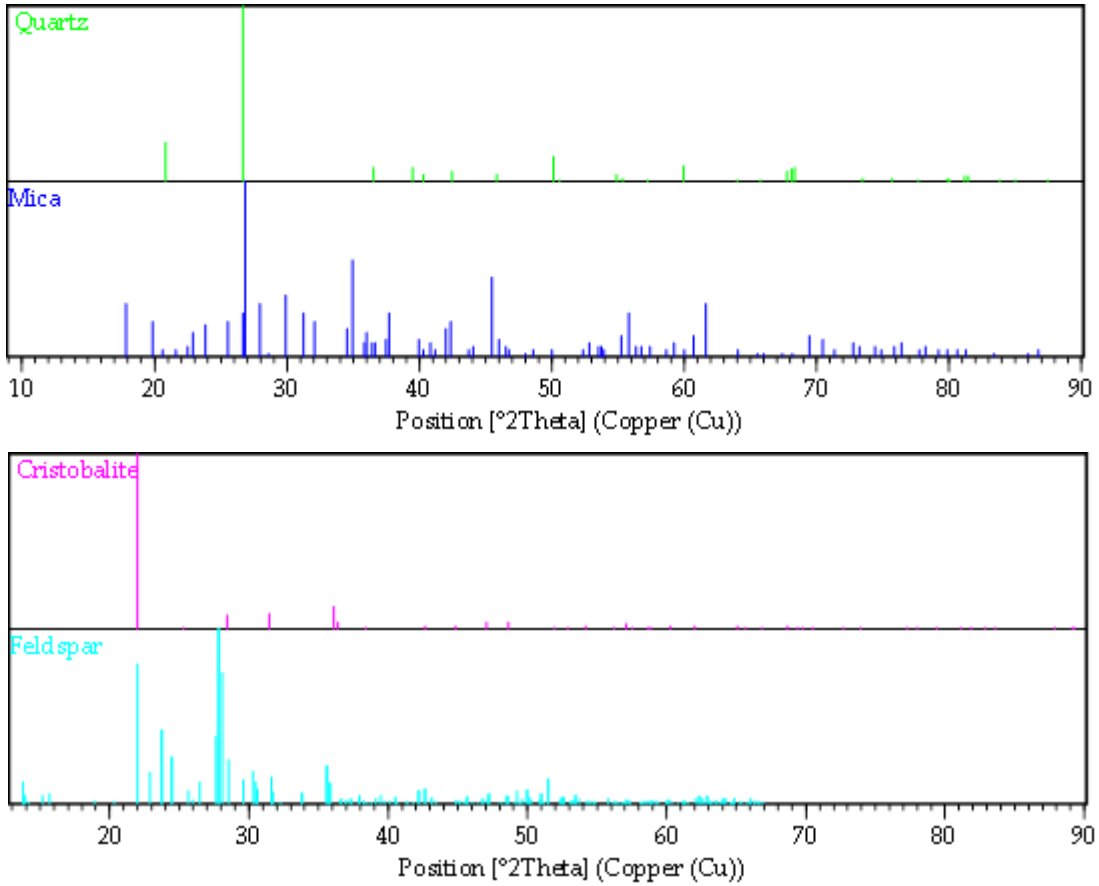
- Create standards from a pure mineral
- Construct a calibration curve
- Compare unknown samples to known standard results to determine silica quantification

Calibration Standard Data



XRD Method Potential Interferences

- Mica*
- Potash
- Feldspars*
- Zircon
- Graphite
- Aluminosilicates



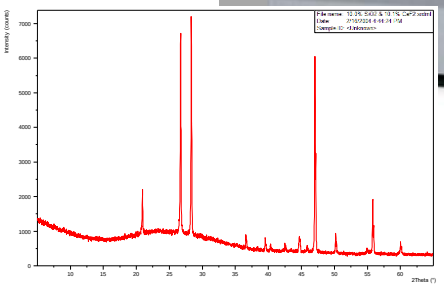
Best way to determine interferences:

collect a bulk settled dust sample or send the bulk material in question for XRD analysis for phase identification.

Bulk - Crystalline Silica Analysis by XRD

- Sample Analysis (in-house method, NIOSH 7500 mod)
  - Drying of sample
  - Matrix reduction / concentration
  - Residue is analyzed for total silica
  - Optional - washed sample analyzed by CCSEM
    - (determination of respirable portion)
  - Panalytical X'pert Pro XRD

- Quality Control
  - Internal Standard Method (CaF_2)
  - ICDD Database for Phase ID
  - Falls under general QSM requirements
    - Training
    - Physical parameter calibrations
    - Maintenance, etc.



Lab Considerations

- Laboratory Selection
  - OSHA Rule Appendix A
  - Sample preparation per method considerations
  - Capability to address interferences
  - Quality assurance and accreditation
  - Detection limits
  - Sampling guidance and support

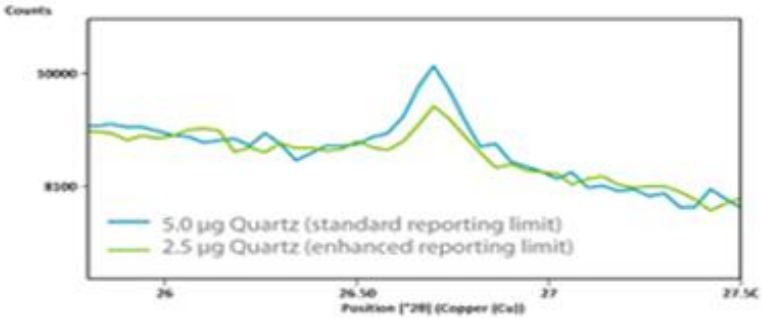


Chart 1. Zoomed-in region of X-ray Diffraction Pattern of Prepared Standards

- Technology Advancement
  - Sample concentration and sampling methods
  - Advances in instrumental analysis / optimization

Chamber Studies

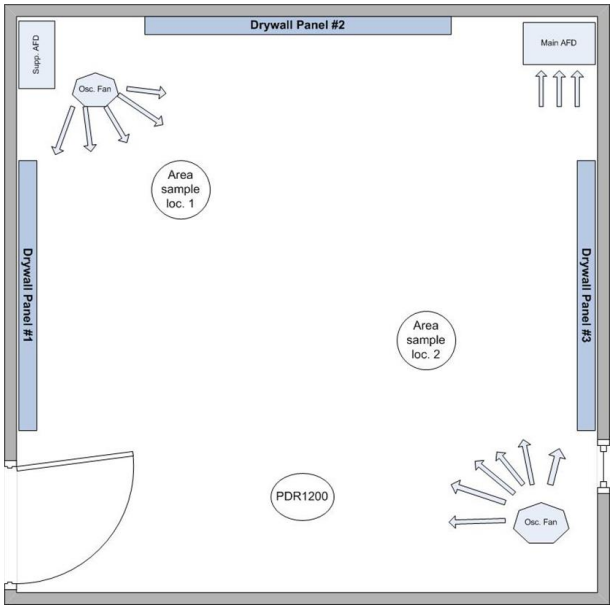
Product Stewardship and RCS

RJLG RCS Chamber Testing

- Animal Feed
- Coal Dust
- Construction Materials
  - Concrete and Cement
  - Siding Products
  - Drywall
  - Joint Compound
- Consumer Products
- Power Tool Comparisons

The Need for Controlled Testing

- Historical Data Gaps
- Relative Indexing of Emissions
- Testing New Products
- Effectiveness of Dust Control
  - LEV
  - Wet Methods
  - Work Procedures / Tools
- Warning and PPE Recommendations
- Validation of Modeling



ACC Study

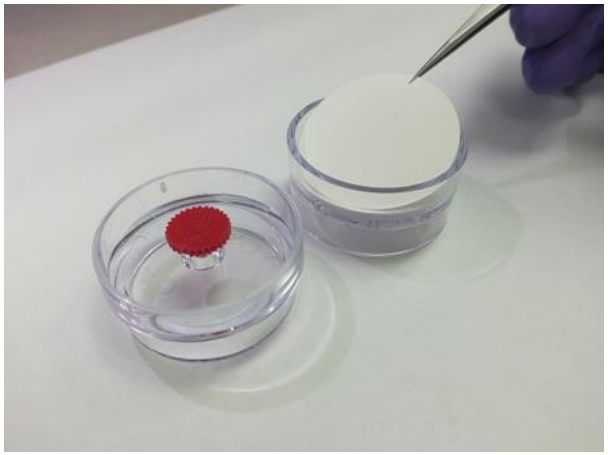
Preliminary Evaluation of Method at Low filter deposits

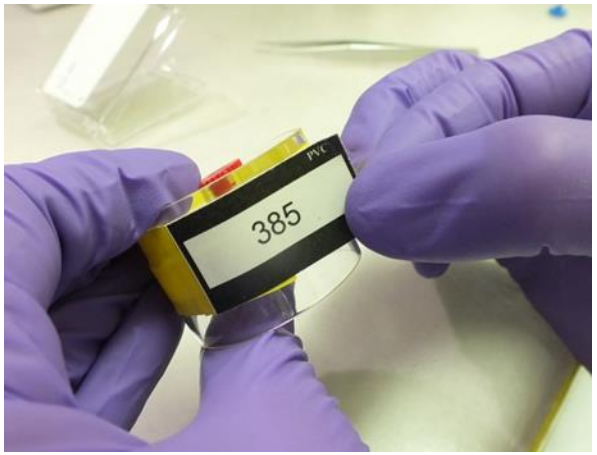
Blind Study

- Sets of 10 samples of known silica loadings
  - Quartz
  - Mixed matrix
    - 50% quartz + 50% kaolinite
    - 50% quartz + 50% feldspar
  - Blanks
- The concentrations correspond to the current PEL, proposed PEL and proposed action limit
  - 0.08 mg/filter (80 µg/filter)
  - 0.04 mg/filter (40 µg/filter)
  - 0.02 mg/filter (20 µg/filter)
- Send samples to labs for NIOSH 7500 analyses

Blind Study - Preparation

- Filters were loaded into cassettes
- Taped and labeled to look like sample cassettes
- Sent to five AIHA accredited laboratories for NIOSH 7500 analysis





Muffle Furnace vs. Plasma Asher

Test	Ashing Device	Crucible	Scraping	Crystalline Silica		
				Standard (μg)	Average (μg)	Average Recovery
1	Plasma	n/a	n/a	19.4	17.3	100.8 ± 4.7%
				48.6	52.3	
				96.1	101.4	
2	Muffle	New	Complete	19.4	14.8	89.8 ± 4.3%
				48.6	43.1	
				96.1	100.1	
3	Muffle	Used	Complete	19.4	15.0	83.0 ± 4.9%
				48.6	41.4	
				96.1	83.2	
5	Muffle	Used	Partial	19.4	14.8	77.4 ± 4.0 %
				48.6	37.9	
				96.1	74.9	
4	Muffle	Used	None	19.4	3.5	49.0 ± 3.8%
				48.6	23.5	
				96.1	77.4	

Thank You.

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