Towards hybrid microfluidic solutions for real-time silica detection in underground coal mines

Silica Exposure and Lung Disease in the Mining Industry Workshop

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Access to facilities at four (UIC/UCB/ANL) campuses

Marvel Nanofabrication Laboratory, UCB  Nanofabrication Central Facility, UIC

Center for Nanoscale Materials, ANL

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Respirable Dust Fraction (ISO) - coal/silica dust

ACGIH/ISO sampling criteria for inhalable, thoracic, and respirable fraction

30 CFR Sub. B

- 1.5 mg/m³ – underground and surface coal mines
- 0.5 mg/m³ – air-intakes and part 90 miners
  - LOD → 100 µg/m³
- 0.1 mg/m³ – quartz, or 10%
  - LOD → 20 µg/m³
WEARDM (Wearable Respirable Dust Monitor)

In development at Air-Microfluidics Group, University of Illinois at Chicago.

Technical specs:

- Large dynamic range (30 µg/m³ – 10 mg/m³)
- Real-time (< 30 min integration at LOD)
- Small
- Low cost (< $1000.00)
- Respirable fraction (4.0 µm 50% cut-point following ISO respirable convention)
- Battery life (250 ml/min flow rate)
- MSHA permissible

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WEARDM (Wearable Respirable Dust Monitor)

- **Ambient air**
- **Elutriator** 10µm cut-point
- **Fractionator** 4µm cut-point
- **Dryer**
- **Dual Fraction Mass Sensor** (QCM & MSR)
- **Exhaust PM_{Fraction}
- **Exhaust PM_{Coarse}
- **PM_{10}
- **PM_{4}
- **Exhaust
Detection principles: Mass-Sensing Resonator (MSR)

\[ \text{Concentration (} mg \cdot m^{-3} \text{)} = \frac{\Delta m (mg)}{\text{Flow rate (} m^3.s^{-1} \text{)} \times \text{time (s)}} \]

**Sauerbrey equation:**

\[ \Delta m = \frac{\Delta f \cdot A \sqrt{\mu_q \rho_q}}{2 f_0^2} \]

\( \Delta f \): frequency change  
\( A \): active sensing area of the crystal  
\( \rho_q \): quartz density  
\( \mu_q \): shear modulus of quartz for AT-cut crystal  
\( f_0 \): resonant frequency of the quartz crystal  
\( \Delta m \): mass added to the crystal’s surface.

**Detection principles:**
- **Mass-Sensing Resonator (MSR)**
Dual Resonator Mass Sensor (DRMS)

**Equation:**

\[
\frac{1}{\lambda} + 4.4\left(\frac{1}{d}\right) + 8.8\left(\frac{1}{d}\right)
\]

**Symbols:**
- \(\rho_a\): Air density
- \(\lambda\): Mean free path at ambient pressure
- \(K_a\): Air thermal conductivity
- \(k_p\): Thermal conductivity of particles
- \(\eta\): Air viscosity
- \(T\): Particle temperature
- \(\nabla T\): Temperature gradient

**Graph:**

Collection efficiency (%) vs. Particle diameter (\(\mu m\))

- Blue: Thermophoretic deposition after inertial impaction (scaled)
- Red: Inertial impaction

**Diagram Details:**
- Inlet
- Outlet
- Quartz crystal microbalance mass sensor resonator
- Heater
- Thermophoresis force

**Notes:**
- \(h\) at ambient pressure
- Conductivity
- Mobility of particles
- Particle temperature
- Gradient
Surface-modification of the MSR: enhanced- inertial impaction

Similarity between the particle capture mechanism of fibrous filter and the pillar enhanced surface
Surface-modification of the MSR: Pillar geometry with 2PP

Response of QCM devices with and without optimized pillar geometry to test aerosols (incense smoke).

Surface-modification of the MSR: Pillar distribution

(a) radially staggered array of circular pillars.
(b) radially staggered array of rectangular pillars.
(c) inline array of rectangular pillars.

(a) Flow field around rectangular fibers. (b) Tangential and normal components of the particle velocity in oblique impaction.

Initial Results

Test aerosol (incense)

Reference monitor (Kanomax 3442)

Initial Results

Cut-point test results with PSL particles.

Histopathology

Coal macule.

Silicotic nodule.
Silica Speciation

• Beer-Lambert Law

Measure of absorbance
transmittance

$A = - \log T = \log \frac{I}{I_0}$

Final light intensity
initial light intensity

Absorptivity
Path length

$A = a(\lambda) b C$

Concentration

$A_{total} = \sum_i a_i(\lambda) b C_i$
Silica Speciation - Optical/Mass Sensor

- Optical sensor is based on diffuse reflectance spectroscopy and beer-Lambert law.

Optical sensor

\[
(2) \quad a_{Si}(\lambda) b \ C_{Si} + a_{Co}(\lambda) b \ C_{Co} + a_b(\lambda) b \ C_b = \log \frac{I}{I_0}
\]

\[
(3) \quad a_{Si}(\lambda') b \ C_{Si} + a_{Co}(\lambda') b \ C_{Co} + +a_b(\lambda') b \ C_b = \log \frac{I'}{I_0'}
\]

Mass sensor

\[
(1) \quad \rho_{Si}C_{Si} + \rho_{Co}C_{Co} + \rho_{b}C_b = M_{QCM}
\]

\[C_{Si}, C_{Co}, C_{b}\]
FTIR Results

Wavelength | Coal | Silica
------------|------|------
2.5 µm     | 70%  | 81%  
3 µm       | 45%  | 83%  

Mix1 - 1:3 silica to coal    Mix2 - 1:4 silica to coal
RAMAN spectroscopy

Bulk silica Sample: Location 0

Bulk 1:1 silica/coal Sample: Location 0
Shortcomings of optical methods w. WEARDM

- **WEARDM sampling at 250 mL/min**
  - Low signal-to-noise at silica LOD
  - Long integration time

- **Confounding signal**
  - Water peak at 2900 nm
  - Kaolin
  - Silica vs. silicates

Liquid microfluidic platform -> chemical detection of cellular toxicity
Silica-inducing cellular damage

- **Silanol groups**
  - Activation of macrophages producing reactive oxygen species
  - Disruption of biological membranes

- **Free radicals**
  - Lipid peroxidation
  - DNA damage
Silica-inducing cellular damage

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  - Lipid peroxidation
  - DNA damage

Colorometric detection
Free radicals - first steps

Role of free radicals in the mechanisms of hemolysis and lipid peroxidation by silica: comparative ESR and cytotoxicity studies.

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FIGURE 3. Effect of “aging” on the silica’s ability to generate hydroxyl radicals, plot A (●) and effect of “aging” of the same sample on the rate of peroxidation of linoleic acid, plot B (○).
Hybrid (air/liquid) microfluidics

- a) deposition/concentration site
- b) reagents, media
- c) Mixing/detection site (optical)
- d) exhaust

- **Air microfluidics**
  - Initial fractionation (respirable)
  - Pre-concentration
- **Liquid microfluidics**
  - Separation concentration
  - Transport
  - Chemical reaction / detection

Seemless transport: digital microfluidics

No voltage - No droplet movement

Droplet movement driven by voltage

Design features that improve pumping:
- Superhydrophobic surfaces
- Dielectric thickness
- Height of top plate
- Material properties/conc. of solution

\[ R_0 = -\frac{2}{d \cos \theta_0} \]

\[ R_d = -\frac{d}{\cos \theta_0 + \cos \theta_d} \]

We found:
\[ \Delta P = \frac{\gamma \cos \theta_s - \cos \theta_0}{d} \]
Bio-Aerosol Detector (Concept drawing)

Legacy PM2.5 sensor design

Adaptation of PM 2.5 design for EWOD pumping based aerosol sampler;

Conclusion

- Difficult to detect silica in real-time (< 30 min integration time) with a wearable footprint using air microfluidics and opto-gravimetric methods
- Established methods exist to detect cellular damaging silica dust in laboratory settings
- Hybrid microfluidic platforms allow for enhanced concentration and chemical detection using legacy methods
- Can be made very low cost:
  - Small footprint
  - Inexpensive materials (i.e. paper)
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