Measuring Aerosol Active Surface Area by Direct Ultraviolet Photoionization and Charge Capture in Continuous Flow

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Low-cost Nanoparticle Sensors

\[ i \propto N \cdot d^{1.1} \]

from diffusion charger

\[ LDSA = \text{[surface area][deposition prob.]} \sim d^2 d^{-1} \sim d^1 \]

NanoTracer - \( N \cdot d^{1.0} \)
NSAM - \( N \cdot d^{1.13} \)
Naneos partector - \( N \cdot d^{1.12} \)
DiSCmini - \( N \cdot d^{1.0} \)

http://www.naneos.ch/
Other Low-Cost Principles: Photo-emission

- Studied since ~1980s
- High charge fraction for small particles
- Responsive to material and surface properties
  - Work function of material, empirical constants
- Photoelectric Aerosol Sensor, EcoChem

\[
\frac{dN^+}{dt} = f(\lambda_{uv}, \pi r_p^2, I_{uv}, F_{PAH}, Y_{PAH}, C_N, t_{irr}),
\]

where
- \(C_N\) = number concentration of particles
- \(N^+\) = positive charged particles
- \(\lambda_{uv}\) = wavelength of the UV-light
- \(I_{uv}\) = photon flux of UV-light
- \(F_{PAH}\) = fraction of coverage of photo-emitting PAH on a particle surface
- \(Y_{PAH}\) = material-dependent photo-electric yield
- \(t_{irr}\) = irradiation time
- \(r_p\) = particle radius
- \(t\) = time.


\[ \alpha^{q\rightarrow q+1} = K_c(h\nu - \Phi^{q\rightarrow q+1})^m \frac{I\pi d^2}{4h\nu} \]

\[ \beta^{q\rightarrow q-1} = D_i \frac{q e^2}{\varepsilon_0 k_B T} \]

Sensor Operating Method
Components of Measured Current

\[ i = c \ YS \]

\[ c = \frac{I}{h\nu} tQe \]

\[ Y = K_c (h\nu - \Phi_\infty)^m \]

\[ S = \pi \sum N_i d_i^2 \]

- Flow rate
- Residence Time
- Electron Charge
- Concentration
- Particle diameter
- Constant for operation
- Work Function (simplified)
- Photoemission Constant
- Quantum Yield
- Empirical Constant for operation
- Surface Area
Objectives

Characterize aerosol using measured current:

a) material type / surface: $K_c, m, \Phi_\infty$

b) concentration, geometric parameters: $N, d_x$

c) morphology

\[ i = c \, YS \]
Aerodynamic Aerosol Classifier (AAC)

- Classifies aerosol source by aerodynamic diameter
- Produces monodisperse distribution (GSD<1.1)
- High transmission efficiency
- No residual particle charge

<table>
<thead>
<tr>
<th>Equivalent Diameter, $d_{eq}$</th>
<th>Force 1, $F_1$</th>
<th>Force 2, $F_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aerodynamic Diameter, $d_a$</td>
<td>Weight/Centrifugal</td>
<td>Drag</td>
</tr>
<tr>
<td>Electrical Mobility Diameter, $d_m$</td>
<td>Electrostatic</td>
<td>Drag</td>
</tr>
</tbody>
</table>
Monodisperse, uncharged:

Soot: $d_m: 40 - 200 \text{ nm}$
N: $3.3 \times 10^4 - 8 \times 10^5 \text{ cm}^{-3}$

Silver agglomerates: $d_m: 20 - 110 \text{ nm}$
N: $1.8 \times 10^4 - 3.8 \times 10^6 \text{ cm}^{-3}$
\[ i = c \ Y N d_m^{2.06} \]

\[ R^2 = 0.98 \]
$i = c \ YN d_m^{2.11}$

$R^2 = 0.97$
Surface Area

Range of mass, effective density (AAC-SMPS)

\[ \rho_{\text{eff}}: 2200 - 5500 \text{ kg m}^{-3} \]

Signal linear with mobility diameter, \( d_m^2 \)

Or, projected area of the agglomerate, \( a_a \)

\[ S = \pi \sum N_i d_i^2 \]
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Material Dependence

\[ Y_{silver} = 3.8 \times Y_{soot} \]

\[ Y = K_c (h \nu - \Phi_\infty)^m \]

\[ h \nu = 6.69 \text{ eV} \]
\[ \Phi_\infty, soot = 4.9 \text{ eV} \]
\[ \Phi_\infty, silver = 4.25 - 4.75 \text{ eV} \]

Both ~linear with \( S \)

\[ i = c Y S \]

NaCl, DOS, Graphene did not ionize

\[ 10 \text{ V} \]
Morphology Dependence

\[ Y_{Ag} = 1.75 \times Y_{Ag, \text{sintered}} \]

Morphology Dependence

\[ Y_{\text{Ag}} = 1.75 \times Y_{\text{Ag, sintered}} \]

Previous literature:

Photo-charging efficiency of silver agglomerates is lower than spheres for the same mobility\(^1\) (2013)

Photo-charging efficiency a function of mobility diameter only, regardless of morphology\(^2\) (2001)

Enhanced photoelectric yield of small (6-15 nm) particles\(^3\)

Interaction with light is the sum of primary particles\(^4\)

Silver aggregates and sintered spheres\(^1\)

\(^1\) Zhou, Zachariah et al., Aerosol Science and Technology. 47, p 672-680 (2013)
\(^3\) Jiang et al., Journal of Applied Physics, 102 (2007)
Characterize the measured current in terms of:

a) material type / surface: $K_c$, $m$, $\Phi_\infty$

b) concentration, geometric parameters: $N$, $d_x$

c) morphology

Recap

$S = \pi N d_s^2$

$Y_{silver} = 3.8 \times Y_{soot}$
Charge Dependent Particle Capture

- Distribution of charges even for monodisperse particles
- Mean is a function of photoionization
- Standard deviation is a function of recombination
- Highly charged or more electrically mobile particles are more likely to be captured

\[ i \propto c_1 N d_S^2 - c_2 N d_S^x \]


\[ d_p: 53 \text{ nm} \]
\[ N: 8.4 \times 10^4 \text{ cm}^{-3} \]
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Two equations and two unknowns

\[ i_1 \approx N d^{2.06}, \; i_2 \approx N d^{2.5} \rightarrow \text{Solve } N^* \text{ and } d^* \]

Silver (AAC)

\[ d_m: 35 - 200 \text{ nm} \]

\[ N: 3.5 \times 10^3 - 2 \times 10^6 \text{ cm}^{-3} \]
‘Pushing the limits’
Noise levels in electrode currents begin to surpass fA resolution required
Scatter due to particle-ion recombination, electric field causing measurements to deviate from two parameter fits.
Diameter and Concentration Estimates

Fitting method appropriate for smaller concentration ranges
3D CFD Model

Particles:
\[ \nabla \cdot (\vec{u}N_q) = \nabla \cdot (D_p \nabla N_q) + \nabla \cdot \left( Z_q \vec{E} N_q \right) + S_{q,\alpha} + S_{q,\beta}\]

Ions:
\[ \nabla \cdot (\vec{u}n_j) = \nabla \cdot (D_i \nabla n_j) + \nabla \cdot \left( Z_j \vec{E} n_j \right) + S_{j,\alpha} + S_{j,\beta}\]

- Upwards of 250+ simultaneous species transport equations each charge state and size bin
- (3D) local resolution of particle charge state (EAC, 2016)
- Agreement with experiment for soot agglomerates (AAAR, Portland, 2016)

Nishida et al., EAC, 2016, Tours, France.
Nishida et al., AAAR, 2016, Portland, USA.
Model

\[ i \propto \pi \sum N_i d_{m,i}^2 \]
Experiment vs Model

$\frac{d^2}{m,s} < 50 \text{ nm}$

Outlet current, $i_o / fA$

Total surface area, $A_p / \text{nm}^2 \text{ cm}^{-3}$

Monodisperse

Polydisperse

Experiment

$175 \text{ V}$
Conclusions

• Signal proportional to total surface area (mobility, $d_m$),
  
  $$S = \pi \sum N_i d_{m,i}^2$$

  of soot and silver nanoparticles for different effective densities and morphologies

• Silver has a higher photoelectric yield than soot $Y_{\text{silver}} = 3.8 \times Y_{\text{soot}}$

• Aggregated silver has higher photoelectric yield than spherical silver

• Potential to estimate concentration, $N$, and surface-weighted mobility diameter, $d_s$, by varying voltage
Acknowledgements

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