Performance of a Personal Thermal Precipitator to Assess Nanoparticle Exposures

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Introduction and background
The increasingly prevalence of nanotechnology

- Products containing nanoparticles rapidly entering marketplace
- Related to this growth, *Personal exposure* to nanomaterials and their toxicity is not well understood.
- Greatest risk is to those working in the nanotechnology sector, but the consumer may be at risk as well (Maynard 2006).
Nanotechnology in Consumer Products

Source: D. Hawxhurst, Woodrow Wilson International Center for Scholars
Incidental nanoparticles are very common

- Primary “nanoparticles” characteristic sizes <100nm (1x10^{-7}m)
- The environment is awash in nanoparticles – natural and artificial, benign to harmful.
- Biogenic and incidental nanoparticles typically outnumber engineered nanoparticles – even in locations where engineered nanoparticles are produced (Tsai et al. 2011)
Common elements between different particle types

Source: RJ Lee Group
Required sampling method specificity

• Personal, breathing-zone sampling is needed

• Method must allow

  Representative collection

  Sizing and counting

  Individual particle elemental composition and / or morphology

• Allow for calculation of exposure
Thermal Precipitation Sampler (TPS)


TPS100 model basic specifications
Type: Personal, breathing zone wearable
Size: 150 x 60 x 35mm
Mass: ~300g
Sample air flow rate: 1 - 10 mL/min (+/- 2% of F.S.)
Battery life: 8+ hrs.
Substrate media: Ferromagnetic electron microscopy grids
Thermal Precipitation Sampler (TPS)

Sample core with flow and temperature controls

Interchangeable sample cartridge holding EM grid

EXPLODED VIEW

Housing with user interface
Removable sample cartridge

Sample air inlet

EM sample grid
Advantages

- Uses EM grid as collection substrate
- Secondary analysis gives size distribution, concentration, and elemental composition
- Thermophoresis is thought benign to particle composition / morphology

Disadvantage

- Not direct-reading - secondary analysis required
- Lower collection rate may challenge very short sample times
Secondary analysis using STEM/ImageJ (Example: Ce-Doped Diesel Exhaust)

Resulting data:
• number density
• size distribution

Source: RJ Lee Group
Single Particle Energy Dispersive Spectroscopy

EDS: Can measure particle elemental composition and bond structure

- Spatial resolution of down to 3nm
- Can be used to identify sub-particle structures (inclusions, etc)

Source: RJ Lee Group
Translating sampled particles to concentration

Personal exposure:
- Concentration
- Size Distribution
- Elemental Composition and morphology

Transfer function:
\[ N(d) = \frac{x(d) F(d)}{Q t S \left( Pt(d) \eta(d) \right)} \]

Sampling with TPS

EM imaging/EDS, post-processing

- number density
- size distribution
- Elemental composition and morphology
Defining the transfer function
Transfer Function

\[
N(d) = \left[ \frac{x(d) A}{Q t S} \right] \left[ \frac{F(d)}{Pt(d) \eta(d)} \right]
\]

\(N(d)\) concentration (number/m\(^3\)) of size range, \(d\)
Ideal Term

\[
\left[ \frac{x(d) \ R}{V} \right]
\]

\(x(d)\)  \(counted\) number of \(collected\) particles of size, \(d\)

\(R\)  ratio of \(total\) EM grid area to \(counted\) area

\(V\)  \(sampled\) air volume (m\(^3\))
Non-ideal term

\[
\left[ \frac{F(d)}{Pt(d) \cdot \eta(d)} \right]
\]

Pt(d) inlet penetration efficiency
\(\eta(d)\) EM grid collection efficiency
F(d) correction for other factors

*All as functions of particle size, d*
Pt(d) – Inlet penetration efficiency

Sample cartridge (cross section)
Pt(d) – Inlet penetration efficiency

Impaction and diffusion losses onto inlet passage surfaces

Sample air…

Sample cartridge (cross section)
Inlet diffusion and impaction loss are experimentally determined:

- Phosphate-buffered saline particles
- $5 \times 10^{10}$ particles/m$^3$
- Grimm SMPS, analyzing particles 20-600nm (size range limited)

$$Pt(d) = \frac{C(d)_{\text{through TPS sample core (unpowered)}}}{C(d)_{\text{direct}}}$$

**Conclusion:** Inlet penetration efficiency is reasonably high and constant
\( \eta(d) \) - collection efficiency to EM sample grid
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*Calculated* via simple consideration of downstream and cross stream velocities

- $V_T$, thermophoretic velocity (Talbot et al. 1980)
- Laminar flow (Re=3)

**Conclusions:**

- Particles concentration expected to be constant
- Size distribution expected to be uniform.
- Expect to analyze any location on the EM grid without introducing bias
F(d) – Correction for other factors

Transfer function now rearranged to solve for remaining term, F(d)

\[ F(d) = \frac{N(d) \ Pt(d) \ \eta(d)}{\left[ \frac{x(d) \ R}{V} \right]} \]
F(d) – Correction for other factors

$$F(d) = \frac{N(d) \cdot Pt(d) \cdot \eta(d)}{x(d) \cdot R}$$

- $N(d)$ - REFERENCE sample concentration (SMPS)
- $Pt(d)$ - Penetration eff. (experiment)
- $\eta(d)$ - EM grid collection efficiency (theory)
- $x(d)$ - Collected & counted particles (STEM and ImageJ analysis)
- $R$ - Ratio of total to sampled EM grid area (geometry)
- $V$ - Volume of sampled air (TPS UI)
$F(d)$ – Correction for other factors

*Similar between locations at most sizes.

- Above unity for $d_{ev} < 70$nm
- Near unity for $d_{ev} > 70$nm
Field Test: How well does transfer function work?
Cerium in Diesel Exhaust: Analysis with TPS and Electron Microscopy

Exhaust dilution tunnel

Automated EM and post-processing

- number density
- size distribution
- Elemental composition and morphology

\[
N(d) = \frac{x(d)}{V} \left( \frac{F(d)}{\text{Pt}(d) \eta(d)} \right)
\]

- Concentration
- Size Distribution

Identify Engineered Nanoparticles

15 nm Cerium inclusion
Particle Size Distribution Measurement of Ce-Doped Diesel Exhaust Using CCSEM

Particle Size Distribution of the Soot Structures

CCSEM and EDS Analysis

75 nm Ce Particle in Soot

Source: RJ Lee Group
Future work

Laboratory studies
  • Sampling mixed incidental and engineering nanoparticles – “needle in haystack”
  • Expanding particle size range of transfer function
  • Improving transfer function for slender aspect-ratio particles (fibers, nanotubes, etc)

Real-world field studies w/ simultaneous SMPS scanning

TPS device development
  • Next-gen device capabilities
  • Miniaturization
  • New / different substrates