Evaluation of data and recommendation on measurement technique and sampling protocol for determining concentrations of engineered and incidental nanoparticles

**Aim**

- To generate and evaluate relevant data to establish appropriate assessment and control methods and identify and prioritize exposure levels;
- To suggest control measures in line with observed exposures scenarios;
- To develop a simple risk assessment tool/checklist to assist managers in the process of health hazard identification and risk prioritization.

**Establish appropriate assessment and control methods**

- **Introduction**
  - Describes
  - Participants (& invitation to interested parties)
  - Material Selected For Studies
  - Approaches & measurement Methods for exposure assessment in work environment.
  - Planned research.

**Participants**

- Main project participants
  - Mintek, a South African State Owned Enterprise (SoE) synthesizes gold nano-particles
  - Eskom, a South African SoE mainly operate coal-powered power stations
  - CSIR, a South African SoE synthesizes various nano-particles
  - NIOH, a South African SoE conducting exposure assessment.

  Interested contributors are welcome to contact:
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  Mary.Gulumian@nioh.nhls.ac.za

**Material Selection**

- To start with, the synthesis process of gold nano-particles is studied first.
Material Selection: Au NPs

<table>
<thead>
<tr>
<th>Test Material</th>
<th>Mean Core Dia.</th>
<th>Capping Agent</th>
<th>By whom</th>
<th>Catalytic activity</th>
<th>Production method</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 14 nm</td>
<td>Citrate</td>
<td>Mintek</td>
<td>CO oxidation</td>
<td>Chemical reduction</td>
<td></td>
</tr>
<tr>
<td>#2 40 nm</td>
<td>Citrate</td>
<td>Mintek</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Au NPs: Major Commercial Uses

- Currently used for Lateral flow diagnostics and Catalysis; Expected to be also applied in Therapeutics (e.g., cancer) and Imaging

AU NPs’ Physicochemical Properties Surface Chemistry

- Multilayer of citrate ions.

Physicochemical properties

- Agglomeration/aggregation/dispersion
- UV/Vis
- TEM

UV/Vis. spectrum of the 14 nm gold nanoparticles. The typical absorption peak of the 14 nm should be between 520-524 nm.

14 nm Au TEM image

- The TEM image of the representative 14nm gold nanoparticles is given.
AU NPs’ behaviour in solutions

- The sharp UV/Vis. absorption spectrum and TEM image clearly indicate that the 14 nm gold nanoparticles do not aggregate in solution.

Physicochemical Properties
Surface Charge

- LM 20 Zetasiser used.
- Measuring -34.8mV.
- This value is sufficient to keep the particles from interacting with each other and therefore maintain a stable particle size.

Physicochemical Properties
Surface Chemistry

- Gel Electrophoresis: separates Au nanoparticles based on size, shape and charge where particles migrate differently depending on molecular weight and charge.

Physicochemical Properties
Redox Potential

- Cyclic voltametry was used.
- CV generally responds to a variety of factors such as pH, solvent, ligand and even if the nanoparticle is bare – it still resembles the bulk gold patterns.

Physicochemical Properties
Octanol/Water Partition Coefficient

- An average of Log $P_{ow} = -2.0$ at about 25 °C using the UV-vis Spectroscopy

Occupational Human Exposure

- Source Emission/Ambient
  - Inhalation.
  - At point of synthesis.
  - Area away from point of synthesis.
Exposure Characterisation in Research Lab

- Walk-Through Survey
  - For possible emission ID
  - Determine frequency & duration of each operation
  - Determine ventilation: General & local exhaust
  - Determine containment breaches in process points

Sampling Strategy

- Background readings.
- Source specific area sampling
- Source specific personal sampling

P-TRAK Ultrafine Particle Counter 8525

Met One HHPC - 6 Airborne Particle Counter

<table>
<thead>
<tr>
<th>Location</th>
<th>Background Particle Counts - P-TRAK</th>
<th>Background Particle Counts - Met One HHPC - 6 Airborne Particle Counter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location A: Fume Hood (1)</td>
<td>44017</td>
<td>14649</td>
</tr>
<tr>
<td>Location B: Bench (2)</td>
<td>38329</td>
<td>12588</td>
</tr>
<tr>
<td>Location C: Fume Hood (3)</td>
<td>36224</td>
<td>12861</td>
</tr>
<tr>
<td>Location D: Bench (4)</td>
<td>31702</td>
<td>11349</td>
</tr>
<tr>
<td>Location E: Fume Hood (5)</td>
<td>40212</td>
<td>11478</td>
</tr>
<tr>
<td>Location F: Bench (6)</td>
<td>34321</td>
<td>10435</td>
</tr>
<tr>
<td>Location G: Bench (7)</td>
<td>27163</td>
<td>9066</td>
</tr>
<tr>
<td>Location H: Freezer (8)</td>
<td>31323</td>
<td>9427</td>
</tr>
<tr>
<td>Location I: Between Benches (9)</td>
<td>23445</td>
<td>8031</td>
</tr>
<tr>
<td>Location J: Between Bench and Far wall (10)</td>
<td>26842</td>
<td>7813</td>
</tr>
<tr>
<td>Location K: In corner of Lab next to “Binder” Machine (11)</td>
<td>23303</td>
<td>7414</td>
</tr>
<tr>
<td>Location L: Next to Balances (12)</td>
<td>27061</td>
<td>7534</td>
</tr>
<tr>
<td>Location M: Electrophoresis Area (13)</td>
<td>27037</td>
<td>6644</td>
</tr>
<tr>
<td>Location N: Unused Fumehood (14)</td>
<td>27399</td>
<td>7431</td>
</tr>
<tr>
<td>Location O: Microwave (15)</td>
<td>31503</td>
<td>8247</td>
</tr>
<tr>
<td>Location P: Bio Imaging System Area (16)</td>
<td>29929</td>
<td>8342</td>
</tr>
<tr>
<td>Location Q: De-Ioniser Bench (17)</td>
<td>27595</td>
<td>7664</td>
</tr>
<tr>
<td>Location R: Entrance of Lab (18)</td>
<td>29998</td>
<td>5998</td>
</tr>
<tr>
<td>Location S: Electro Chemistry Room (19)</td>
<td>2575</td>
<td>537</td>
</tr>
<tr>
<td>Location T: Diagnostics Room (20)</td>
<td>2897</td>
<td>528</td>
</tr>
<tr>
<td>Location U: Tissue Culture Room (21)</td>
<td>3801</td>
<td>709</td>
</tr>
<tr>
<td>Location V: Corridor Outside Lab (22)</td>
<td>32290</td>
<td>8209</td>
</tr>
</tbody>
</table>

The inter-leading corridor

- These two instruments give the counts of the particles without their characterization.
Collection of particles for characterization

- Selects a wide-range sampler: 2 nm up to 20 μm.
- Particles are collected simultaneously and separated into 12 size channels.
- It can give:
  - The size-resolved structure.
  - Mass-resolved size distributions.
  - Morphology.
  - Chemical composition of captured particles.
  - Determines the concentration of the Engineered Nanoparticles against a background of naturally occurring aerosols and other anthropogenic aerosols produced from processes such as combustion.
- For example, engineered nano-silver has been detected at levels of 2 ng/m³ against a background aerosol concentration of >40 μg/m³.

Physicochemical properties

- Aerodynamic diameter
- Particle number
- Size
- Surface area

Instrument used

- TSI Scanning Mobility Particle Sizer (SMPS), MODEL 3080, for particle number size distribution:
  - Differential Mobility Analyzer (DMA) coupled in series with a CDC
    - DMA, MODEL 3081+ selects particle size interval of sampled aerosol
    - Condensation Particle Counter (CPC), MODEL 3372 = counts particles exiting the classifier
  - Particles neutralised @ DMA inlet with radioactive sources (Kr85, Am241) to reach charge equilibrium
  - Electric Field Scanning to different particle sizes selected for particle size distribution
  - APS 3321 (Aerodynamic Particle Sizer)

The histogram shows a combined data from a TSI APS (Model 3321) and TSI SMPS (consisting of an Electrostatic Classifier, Model 3080 and Condensation Particle Counter, Model 3372)

Physicochemical properties (cont.)

- Chemical analysis
  - ICP-MS
- Size and agglomeration stage
  - TEM
- Surface properties/Ligands
  - FT-IR
  - NMR
- Surface activity
  - ESR

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• Thank you for your attention