Carbon Nanotubes

Sampling and Analysis

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Nanoparticles

Definition

• A particle that is usually less than 100 nm or has one dimension less than 100 nm.
Nanoparticles

100 nm

58,000 x

160 nm
Nanoparticles

Uses

- Medicine
- Material science
- Manufacturing
- Electronics
- Energy
- Sports equipment
- Aerospace
Carbon Nanotubes
Carbon Nanotubes

- High length to width aspect ratio
- High tensile strength
- Relatively easy to manufacture
- Economical
Carbon Nanotubes

Chrysotile

CNT

72,000x

150 nm
Carbon Nanotubes

Potential Health Issues and Benefits

• Similar concerns to asbestos exposure
• Can CNTs cause the same diseases as asbestos?
• Potential uses in cancer treatment, neuroscience, infection therapy, tissue regeneration
• CNTs and the blood brain barrier
Functionalized CNTs

- This simply means to bond something to the surface of the CNT
- It is easy to bond other elements to carbon
- CNTs can have a high cytotoxicity.
- Functionalization can remove that danger.
Functionalized CNTs
Carbon Nanotube Products
Analytical Methods

• NIOSH 5040
• Modified asbestos in air methods
• In development ASTM method
NIOSH 5040
Elemental Carbon

• April 2013 – CDC and NIOSH propose a regulatory exposure limit of 1 μg/m³ elemental carbon as a resparable mass 8-hour time-weighted average (TWA) concentration

• Other types of elemental carbon such as diesel soot or carbon black cannot be present.

• Collect samples on a 37mm quartz fiber filter.

• Thermal-optical analysis
Modified Asbestos Methods

- Collect samples on 25mm 0.45 μm MCE filters
- AHERA, ISO 10312, ASTM 6281, NIOSH 7402
- Discard the minimum lengths
- Keep the length/width ratio
- Increase the magnification to 50,000x
- Change the area analyzed
Releasability Study

To determine via TEM methods the airborne release of carbon nanotubes (CNT) while manipulating composite materials

• Analytical Methods:
  – ISO 13794 / Modified ASTM 6281
  – In development ASTM CNT method
Materials Studied

- Composite plastic with CNT in the matrix
- Size 100 cm x 100 cm x 6 cm
Materials Studied

• Woven synthetic cloth
• Size 100 cm x 100 cm (total)
Methods of Handling

• Work done in pre-cleaned glove box configured with two sampling ports (Left and Right)
• Size: 1 m x 0.7 m x 0.7 m
Methods of Handling

• Composite
  – Drilling
  – Hand Sanding
  – Power Cutting
• Synthetic Cloth
  – Compressed Air
  – Impact Hammer
  – Cutting with Scissors
Methods of Handling

• Composite: Drilling
  – 13 holes in 30 mins. 3/16” and 5/32”
Methods of Handling

• Composite: Hand Sanding
  – 60-grit sandpaper mounted on wood block
  – 11 mins. of sanding
Methods of Handling

• Composite: Power Cutting
  – 4.5-inch rotary saw
  – One 100cm cut and Two 1cm cuts
Methods of Handling

- Synthetic Cloth: Compressed Air Blowing
  - 5-mins. from various directions
Methods of Handling

- Synthetic Cloth: Impact Hammer
  - 10-mins. Using both ends of a ball peen hammer
Methods of Handling

• Synthetic Cloth: Cutting with Scissors
  – Multiple cuts in multiple directions for 15-mins.
Sampling Parameters

- High Volume Sampling Pumps
- Sampling rates between 9 and 12 L/min
- 0.45 µm MCE (TEM) Cassette

<table>
<thead>
<tr>
<th>Material/Task</th>
<th>No. of Samples Collected</th>
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</thead>
<tbody>
<tr>
<td>Composite/Drill</td>
<td>2</td>
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<tr>
<td>Composite/Hand Sanding</td>
<td>4</td>
</tr>
<tr>
<td>Composite/Power Cutting</td>
<td>4</td>
</tr>
<tr>
<td>Synthetic Cloth/Air Blow</td>
<td>2</td>
</tr>
<tr>
<td>Synthetic Cloth/Hammer</td>
<td>2</td>
</tr>
<tr>
<td>Synthetic Cloth/Scissor Cut</td>
<td>2</td>
</tr>
</tbody>
</table>
Analytical Methods

A. ISO 13794 / Modified ASTM 6281
B. In development ASTM CNT method
ISO 13974 / Modified ASTM 6281

- ISO 13794 used for indirect preparation of overloaded samples.
- ASTM 6281 – Modified by changing the 0.5 um (500 nm) minimum length to 100 nm with a 5:1 aspect ratio.
- ASTM 6281 – Modified by changing the analytical magnification from 20,000x to 58,000x.
- Allows for enhanced counting of complex structures.
ASTM CNT Method

• Minimum length of 250 nm
• Aspect Ratio of 3:1
• Similar to AHERA structure counting criteria
• Examine the grid at 20,000x increasing to at least 50,000x on suspect structures
Composite Material

58,000x

100 nm
Composite Material

- Multi-walled nanotubes
- Dense matrices
- Width of 15 to 20 nm
- Very few individual tubes seen
- Some structures between 100 nm and 250 nm in length
Composite Material

250 nm  36,000x
Composite Material

100,000x 100 nm
Composite Material

29,000x

200 nm
## Composite Material Results

<table>
<thead>
<tr>
<th>Sample</th>
<th># structures</th>
<th>CNT/cc</th>
<th># structures</th>
<th>CNT/cc</th>
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<tbody>
<tr>
<td>Drilling 1</td>
<td>49</td>
<td>122</td>
<td>35</td>
<td>87</td>
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<tr>
<td>Drilling 2</td>
<td>35</td>
<td>87</td>
<td>28</td>
<td>69</td>
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<tr>
<td>Sanding 1</td>
<td>7</td>
<td>26</td>
<td>6</td>
<td>22</td>
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<tr>
<td>Sanding 2</td>
<td>8</td>
<td>22</td>
<td>8</td>
<td>22</td>
</tr>
<tr>
<td>Cutting 1</td>
<td>15</td>
<td>207</td>
<td>12</td>
<td>166</td>
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<tr>
<td>Cutting 2</td>
<td>14</td>
<td>194</td>
<td>9</td>
<td>124</td>
</tr>
</tbody>
</table>

**ASTM 6281**

**ASTM CNT Method**
Synthetic Cloth
Synthetic Cloth

- Multi-walled CNTs
- Matrices and numerous complex structures
- Individual fibers.
- Larger CNTs than the composite material
Synthetic Cloth

1 μm

3,600x
Synthetic Cloth

100 nm

58,000 x
Synthetic Cloth

100,000x

100 nm
## Synthetic Cloth

<table>
<thead>
<tr>
<th>Sample</th>
<th>ASTM 6281 # structures</th>
<th>CNT/cc</th>
<th>ASTM CNT Method # structures</th>
<th>CNT/cc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air 1</td>
<td>387</td>
<td>282</td>
<td>336</td>
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<td>Air 2</td>
<td>402</td>
<td>322</td>
<td>342</td>
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<td>Impact 1</td>
<td>103</td>
<td>17.8</td>
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<td>15.9</td>
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<td>Impact 2</td>
<td>115</td>
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<td>Cutting 1</td>
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<td>37.1</td>
<td>201</td>
<td>34.1</td>
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<tr>
<td>Cutting 2</td>
<td>188</td>
<td>35</td>
<td>181</td>
<td>33.7</td>
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</tbody>
</table>
Analytical Conclusions

• 20,000x is not high enough magnification for some structures
• Depending on the CNTs and the material the cutoff of 250 nm may be too large.
• Very dense matrices and clusters may not be counted by either method.
• ASTM 6281 had higher counts than the CNT method.
Summary

- CNTs can be both a health hazard and a benefit
- Analytical methods exist or are in development but need some work
- There isn’t a comprehensive method that will tell you everything about any CNTs present
- Functionalized CNTs can overcome some of the potential health hazards.