Differentiation of Carbon Nanotube and Particulate Matter Contamination on Workplace Surfaces using microProbe Raman Spectroscopy

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Carbon Nanotube (CNT) Production Facility

- CNT manufacturers produce CNTs at a capacity of 100 – 500 tons/year

Carbon Nanotubes Produced at Hythane

SouthWest Nanotechnologies Inc., Norman, OK
Applications of Carbon Nanotubes

- CNTs may be used in advanced nanocomposites in packaging, as field-effect transistors, or as interconnect materials.
Potential Occupational Hazards of CNTs

- CNT exposure is not a major concern once CNTs are incorporated into a stable matrix.

- CNT exposure routes:
  - Inhalation
  - Ingestion
  - Absorption

- Highest exposures are likely to occur during handling of the dry powder (collection, weighing, blending, and transferring to containers) and during maintenance of reactors, balances, and other equipment.

UTD Concern: Weighing CNT Powders to Make CNT Solutions
12-Page Standard Protocol for Weighing CNTs and Carbon Nanoparticles

I. Safe Handling Practices

II. Decontamination of Work Areas

III. Personnel Decontamination

IV. Disposal of Waste
Project Goal

- Design a rapid, sensitive, and selective method to sample and test for the presence of CNTs on workplace surfaces where raw materials are handled.

- Factors to Consider
  1. Choice of instrument
  2. Selection of a technique to sample surfaces
Single-Walled Carbon Nanotubes (SWNTs) Have a Number of Unique Raman Signals

Radial Breathing Modes (RBMs)

D-Band ("Disordered" Carbon)

G-Band

G+ Band

G’-Band

SOM

Raman Intensity

Wavenumber (cm\(^{-1}\))

150 250 350 1200 1600 2000 2400 2800
Advantages of Raman Spectroscopy

- There are a number of resonances common to all sp\(^2\) carbon systems that can be used to unambiguously confirm the presence of sp\(^2\) nanocarbons (i.e., CNTs, graphene oxide, graphene, graphite, and most amorphous carbon materials) in a sample.
Advantages of Raman Spectroscopy

The second advantage is that the spectral features of these resonances, in particular, the G- and G’-bands at ~1582 cm\(^{-1}\) and ~2600 cm\(^{-1}\) respectively, can be used to distinguish one CNP from another.

[MS Dresselhaus et al., Nano Letters. vol. 10, issue 3 (2010) 751-758]
Confocal microProbe Raman Spectrometer

Direct, Label-Free Detection of CNTs

Horiba Jobin Yvon
- 632.8 nm Laser
  - Spot size < 2 μm
- Confocal Pinhole
  - Size = 400 μm
- 50x objective
  - NA = 0.75
Selection of Surface Sampling Technique

Quartz Fiber Filter Paper (1” Diameter)

Suitable for use in U.S. EPA Air Monitoring Systems
National Institute for Occupational Safety and Health (NIOSH) Recommendations

- NIOSH recommends that exposures to CNTs be kept below the recommended exposure limit of 1 µg/m³ of air.

- To put this in perspective, the permissible exposure limit for graphite is 5,000 µg/m³, and that for carbon black is 3,500 µg/m³.

- Last year, the recommended exposure limit for CNTs was decreased from 7 µg/m³ to 1 µg/m³ of air.
Limit of Detection Experiment
Is this Method Sensitive Enough?

Known amounts of SWNTs were weighed out on a nanobalance.

Placed on a white surface.

Collected with quartz fiber filter paper.
Dry Particle Analysis of SWNTs

A

B

C
Dry Particle Analysis of SWNTs

633-nm Raman Laser Beam
Representative 633-nm Raman Spectrum from a 2.5-µg Dry SWNT Particle

Sub-microgram (µg) Limit of Detection
Carbon Nanotubes or Particulate Matter?

Is this Method Selective Enough?
633-nm Raman Spectrum of Dark Material from Under the Balance
Material From Under the Balance

SG-76 SWNT Standard

Raman Shift (cm\(^{-1}\))

Intensity

Raman Shift (cm\(^{-1}\))

Intensity

G-

RBM\text{s}
633-nm Raman Spectrum of Dark Material from Back Corner of Balance Table

Intensity

Raman Shift (cm\(^{-1}\))

- RBMs
- D
- G-
- SOM
- G+
- G’
SG-76 SWNT Standard

Material from Back Corner of Balance Table
633-nm Raman Spectrum of Dark Material from a Table Across the Room

Yes, this Method is Selective
CNT Contamination Cannot be Visually Detected!
National Institute for Occupational Safety and Health (NIOSH) Recommendation

1 µg/m$^3$ elemental carbon as a respirable mass 8-hour time weighted average concentration

[Occupational Exposure to Carbon Nanotubes and Nanofibers: NIOSH, 2013].

Why is this a recommendation and not a regulation?

- **Conflicting reports in literature about CNT toxicity.**

- **There is a lack of contamination data from laboratories or worksites in which nanomaterials are handled.**
How Widespread is the CNT Contamination?
How Widespread is the CNT Contamination?
How Widespread is the CNT Contamination?

![Graph showing Raman Shift vs. Intensity](image)

- **SOM**: 
- **G+**: 
- **D**: 
- **G-**: 
- **RBMs**: 
- **G’**: 

Raman Shift (cm$^{-1}$) 

Intensity
SG-76 SWNT Standard

Material From Ledge of Chemical Vapor Hood
Conclusions

- µg amounts of SWNTs were detected on workplace surfaces
  (Note: Air sampling tests have not been performed.)

- Graphene, Graphene Oxide, and MWNT Users 😃
What’s Next?

- Improve user safety training
- Periodically monitor user safety compliance
- Periodically analyze workplace surfaces, as well as, neighboring surfaces, walls, etc.
- Develop new instrumentation for the automated, unattended analysis of multiple quartz filter papers
alpha 300R scanning confocal Raman microscope with 532-nm and 785-nm laser excitation
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