


November 14, 2013

ERC TeleSeminar Series



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

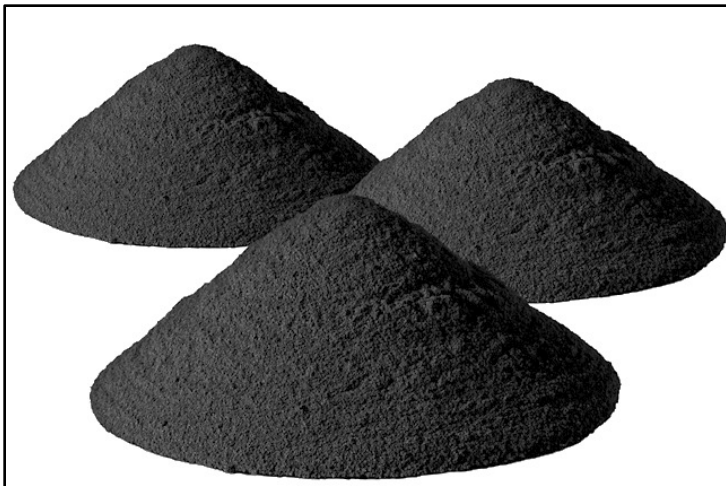
Michael Yukica

Bionanosciences Group



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

Li-Ion Batteries



Sporting Goods



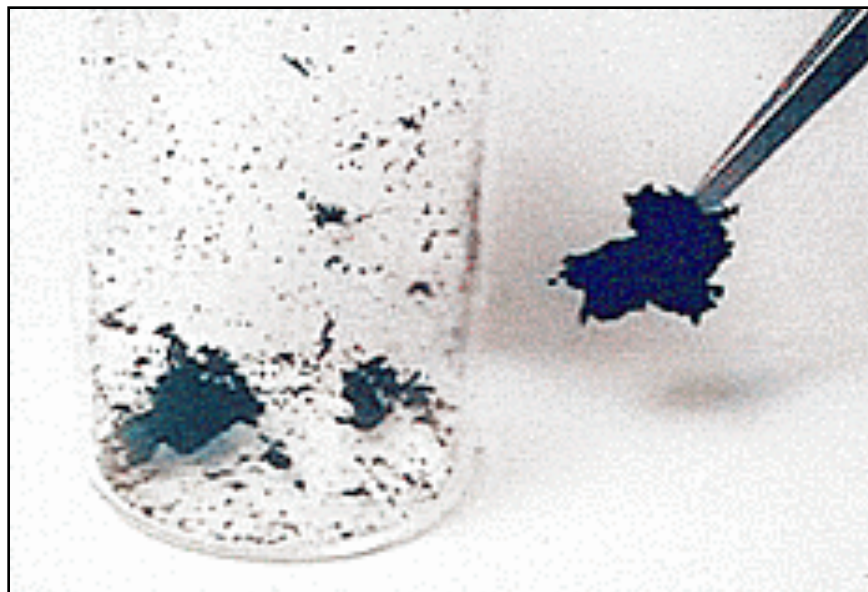
Electronics



- 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.



[C.M. Long et al., Environmental Pollution, vol. 181 (2013) 271-286]

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

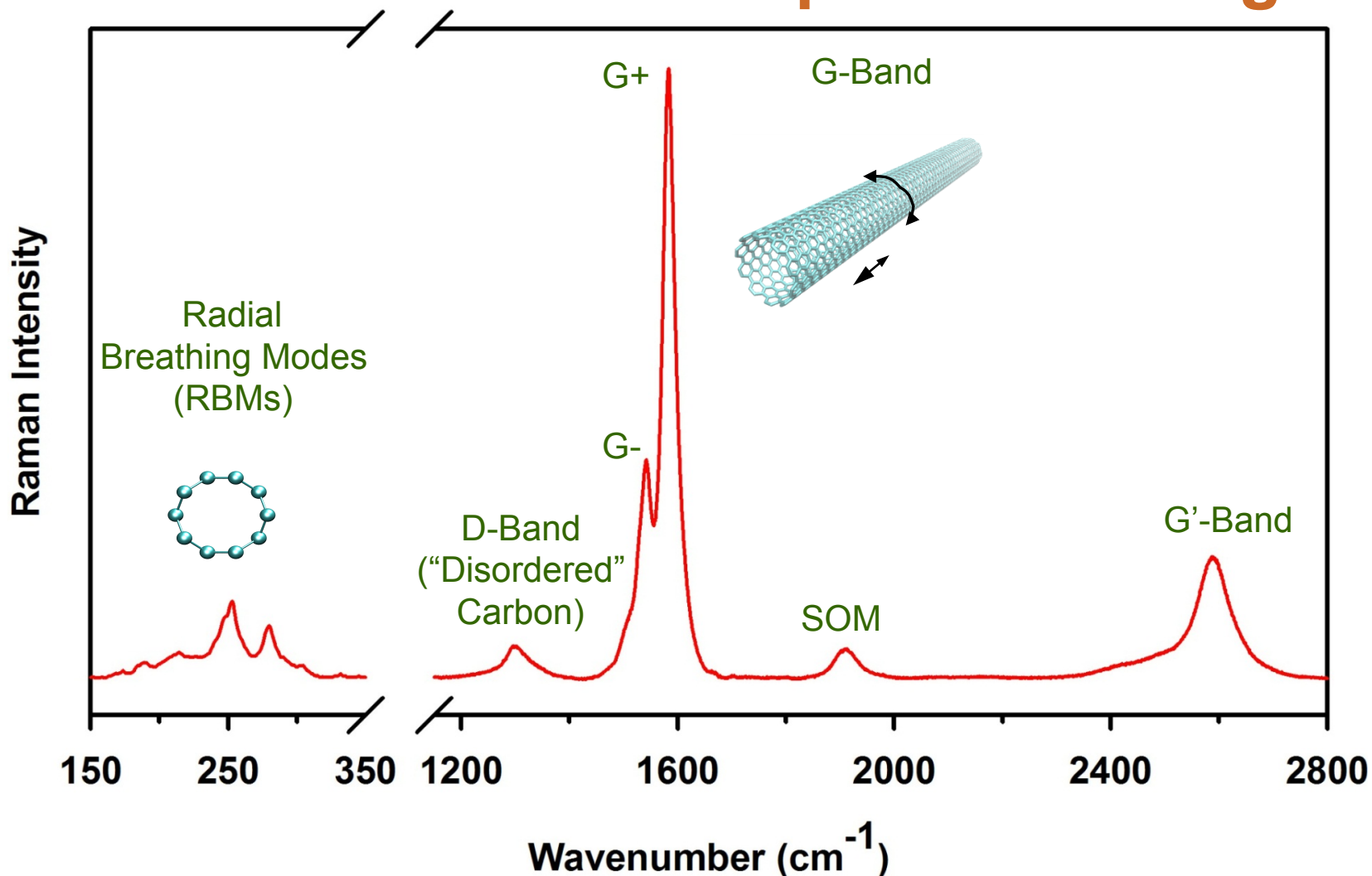
Project Goal

- **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

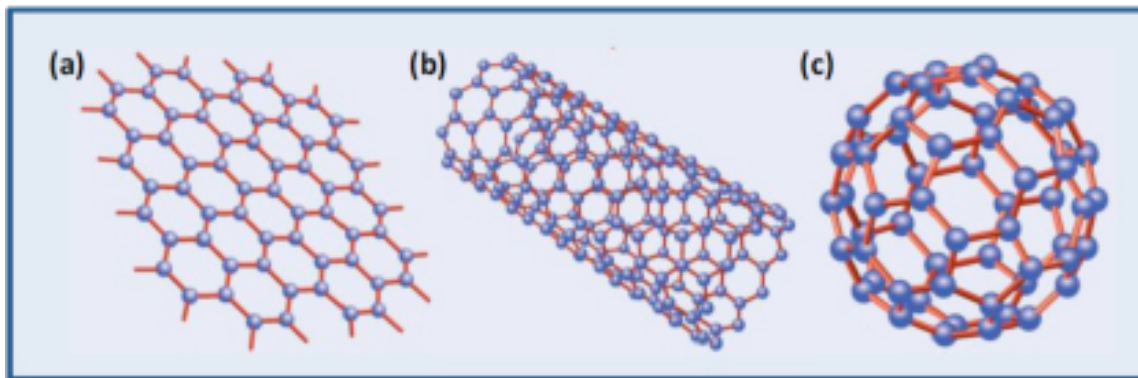


Single-Walled Carbon Nanotubes (SWNTs) Have a Number of Unique Raman Signals



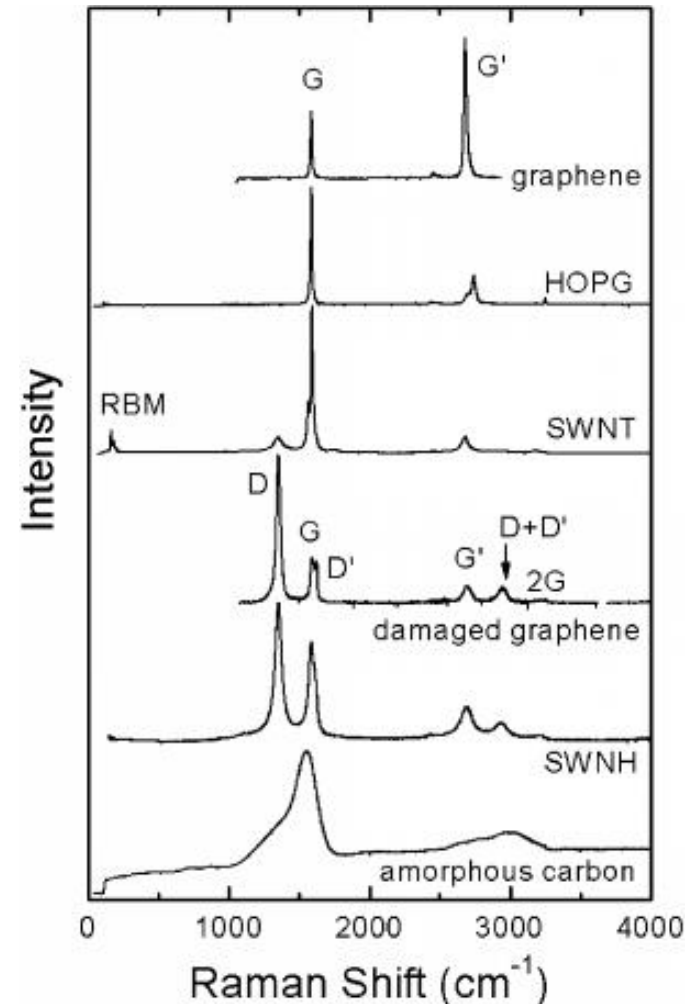
Advantages of Raman Spectroscopy

- 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 $\sim 1582 \text{ cm}^{-1}$ and $\sim 2600 \text{ cm}^{-1}$ respectively, can be used to distinguish one CNP from another.

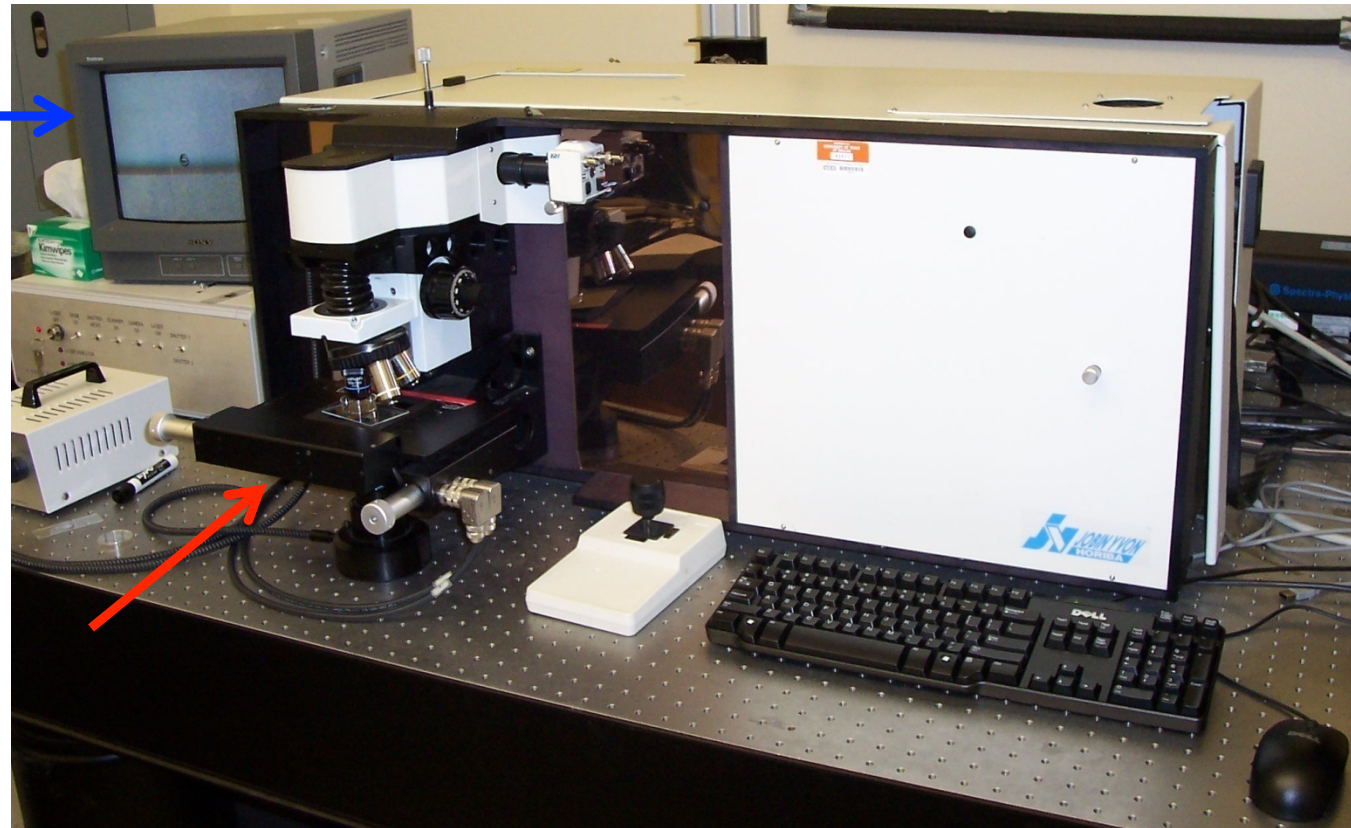


Confocal microProbe Raman Spectrometer

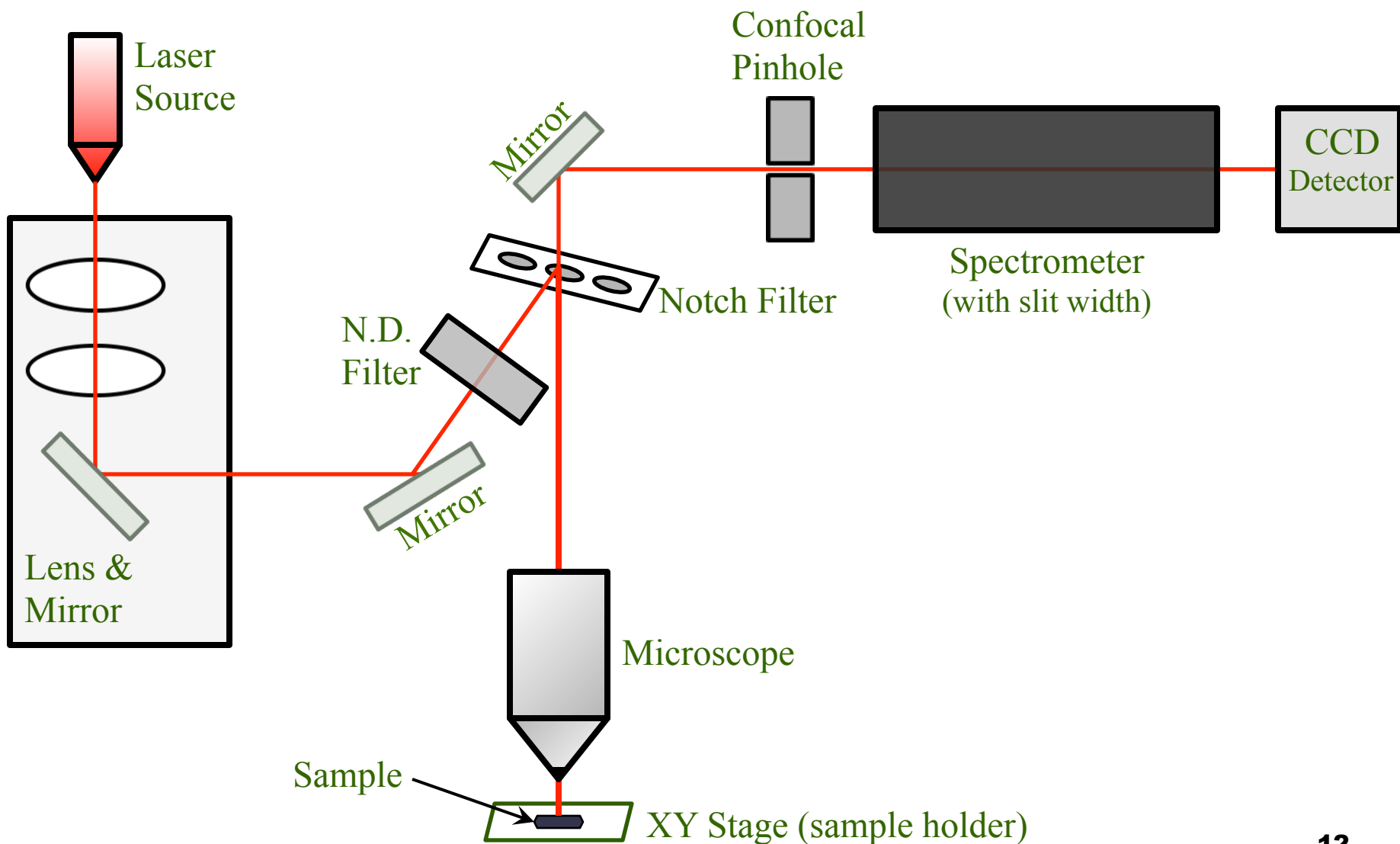
Direct, Label-Free Detection of CNTs

Horiba Jobin Yvon

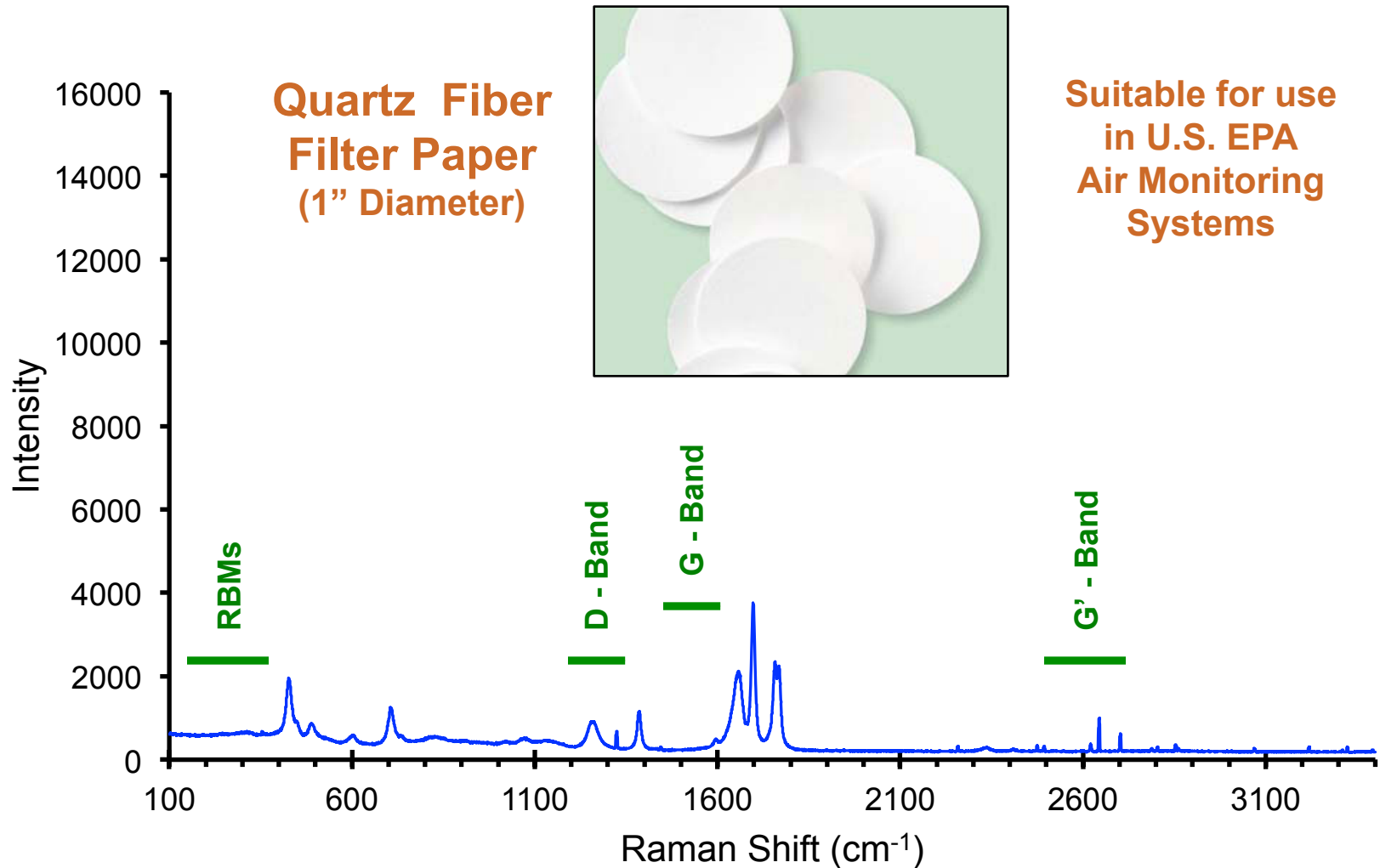
- 632.8 nm Laser
 - Spot size < 2 μm
- Confocal Pinhole
 - Size = 400 μm
- 50x objective
 - NA = 0.75



Confocal microProbe Raman Spectrometer



Selection of Surface Sampling Technique



National Institute for Occupational Safety and Health (NIOSH) Recommendations

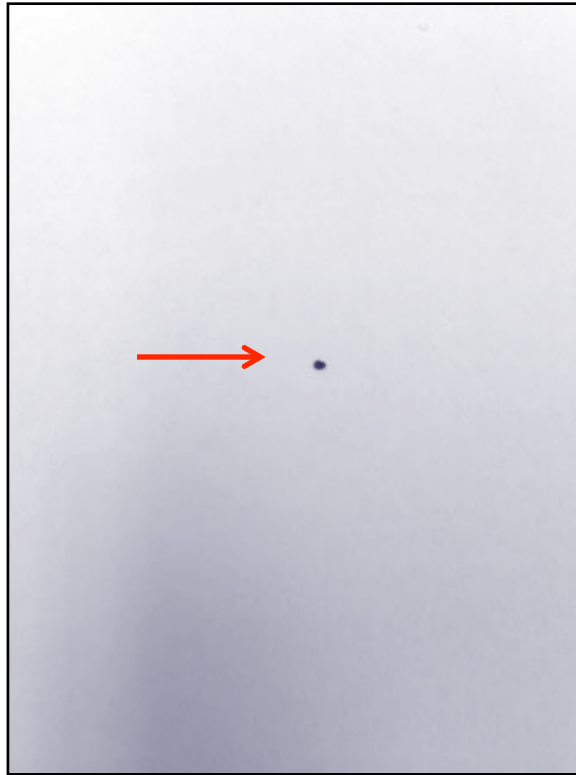
- NIOSH recommends that exposures to CNTs be kept below the recommended exposure limit of **1 $\mu\text{g}/\text{m}^3$ elemental carbon as a respirable mass 8-hour time weighted average concentration.**
- To put this in perspective, the permissible exposure limit for graphite is $5,000 \mu\text{g}/\text{m}^3$, and that for carbon black is $3,500 \mu\text{g}/\text{m}^3$
- Last year, the recommended exposure limit for CNTs was decreased from $7 \mu\text{g}/\text{m}^3$ to $1 \mu\text{g}/\text{m}^3$ of air.

Limit of Detection Experiment

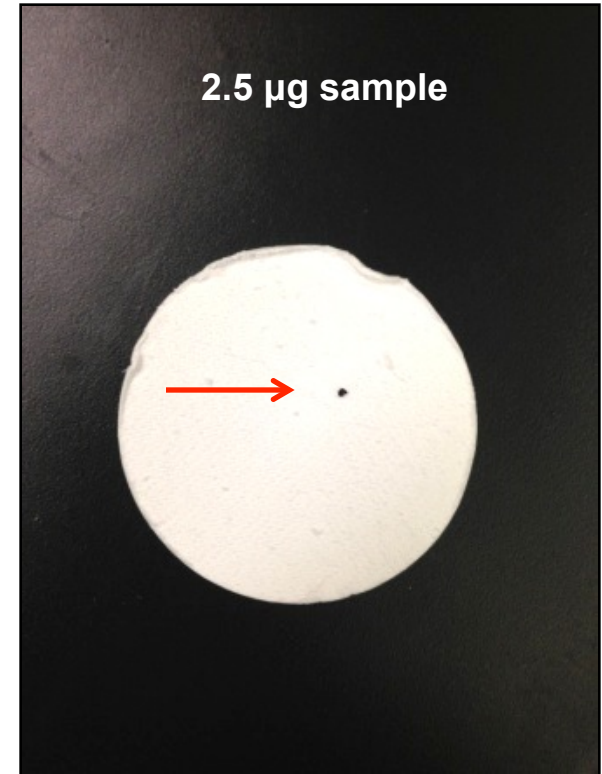
Is this Method Sensitive Enough?



Known amounts of SWNTs were weighed out on a nanobalance.

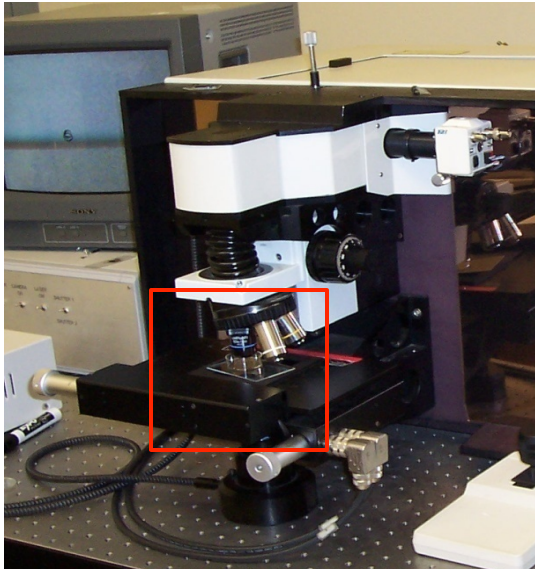
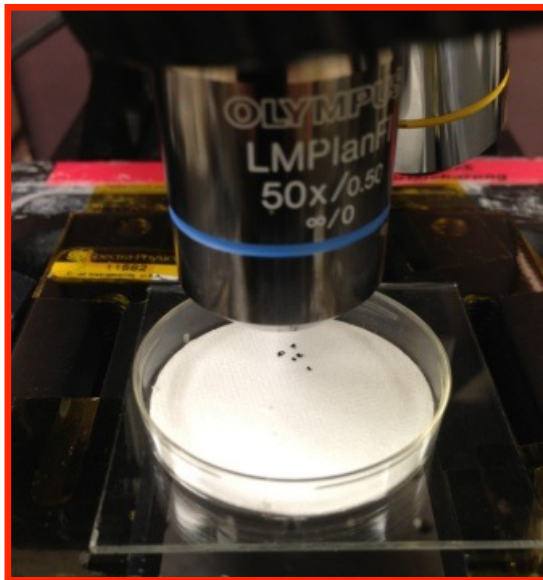


Placed on a white surface.



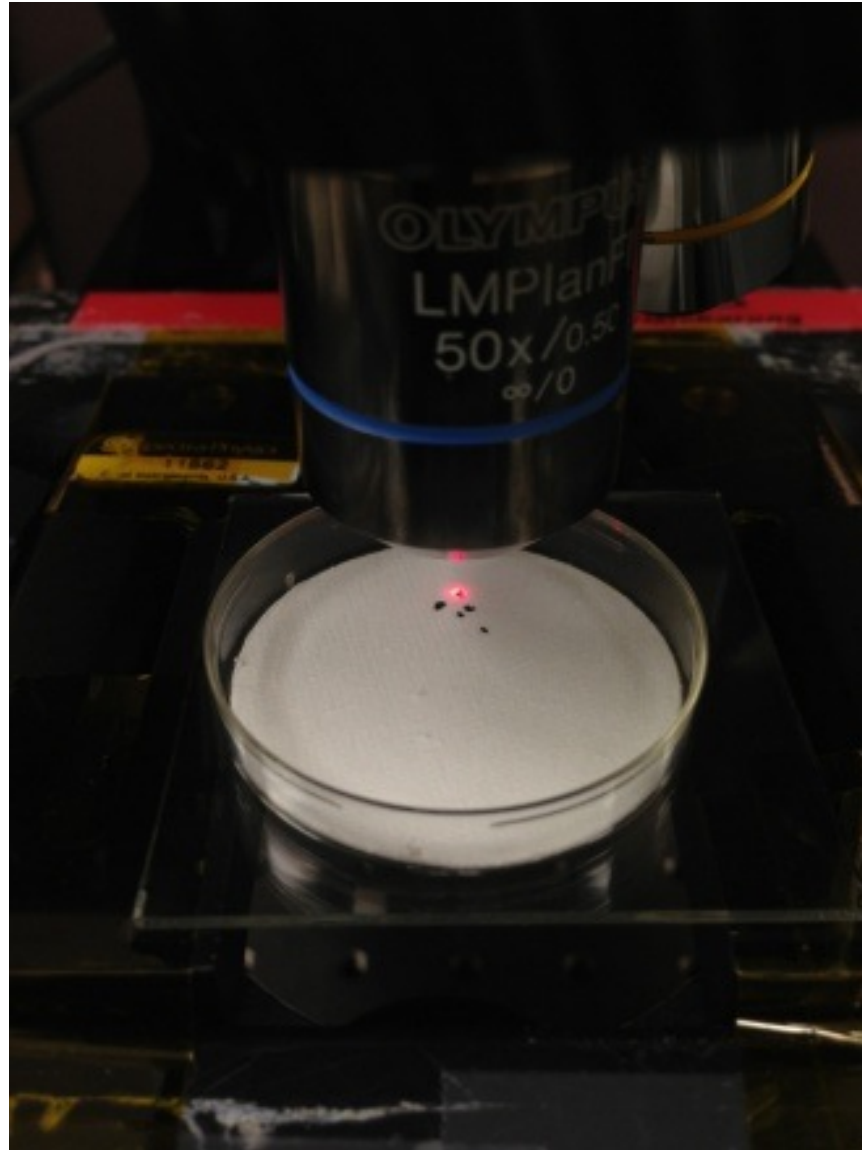
Collected with quartz fiber filter paper.

Dry Particle Analysis of SWNTs

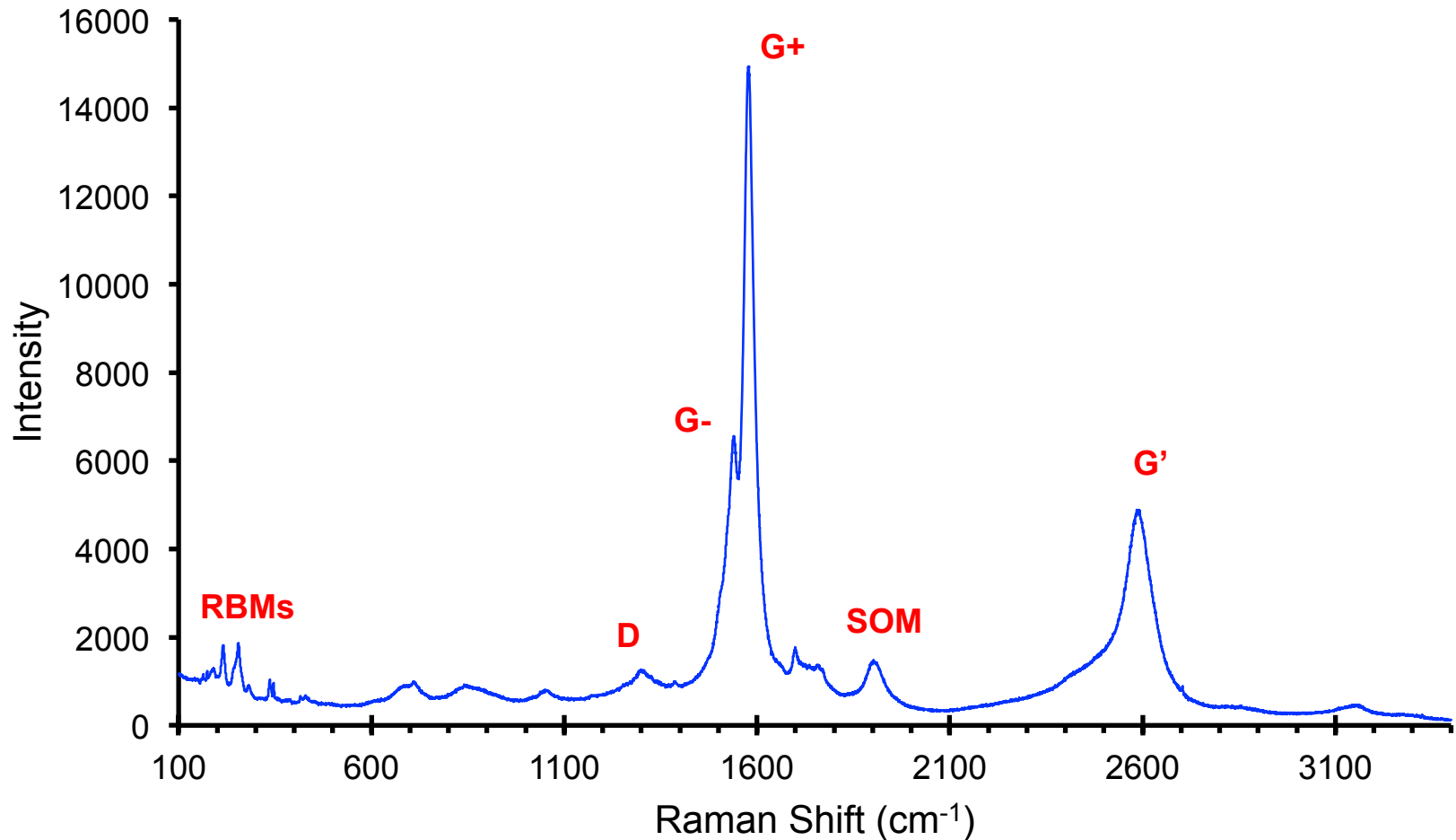
A**B****C**

Dry Particle Analysis of SWNTs

633-nm
Raman Laser
Beam



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

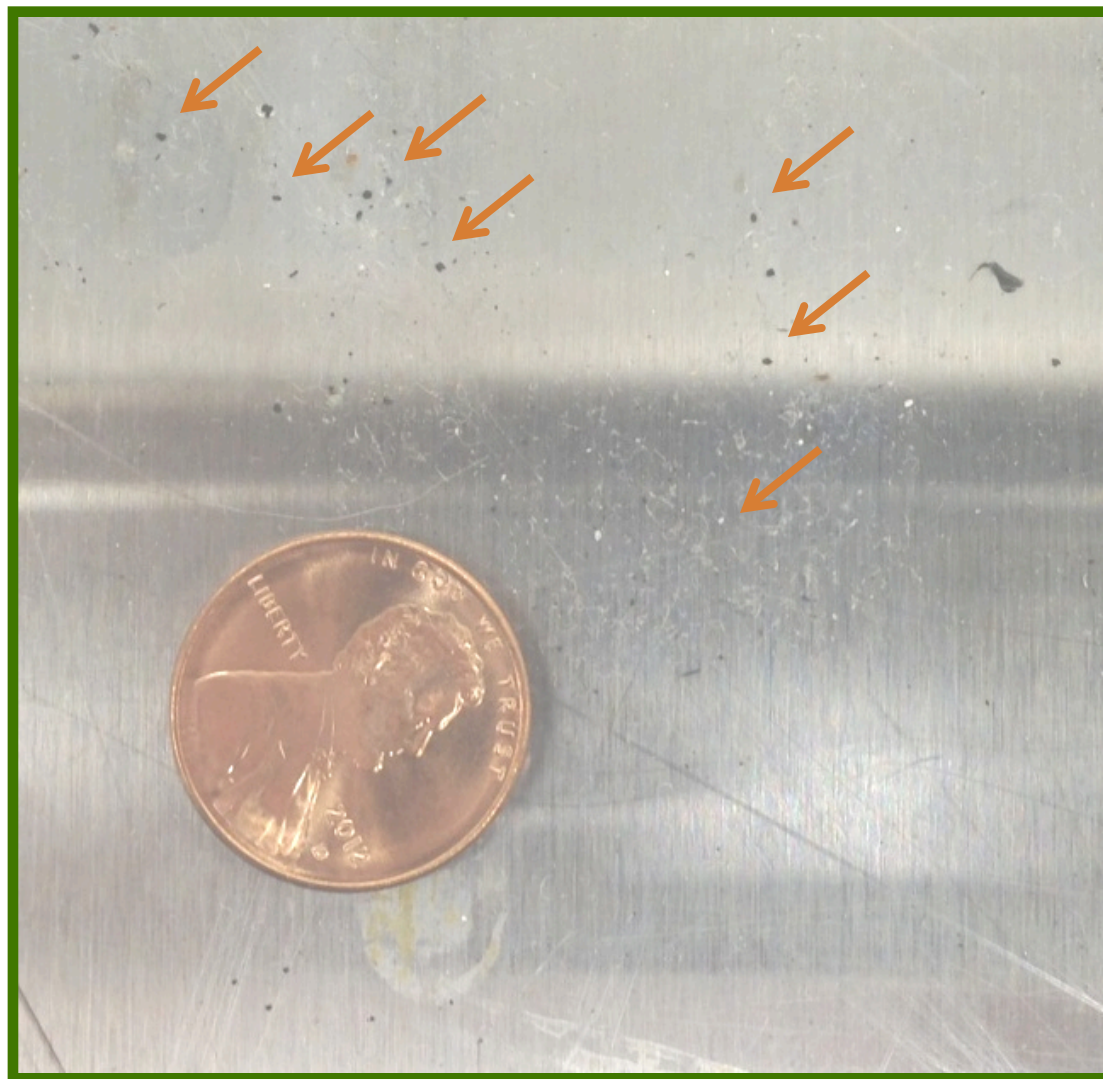


Sub-microgram (μg) Limit of Detection

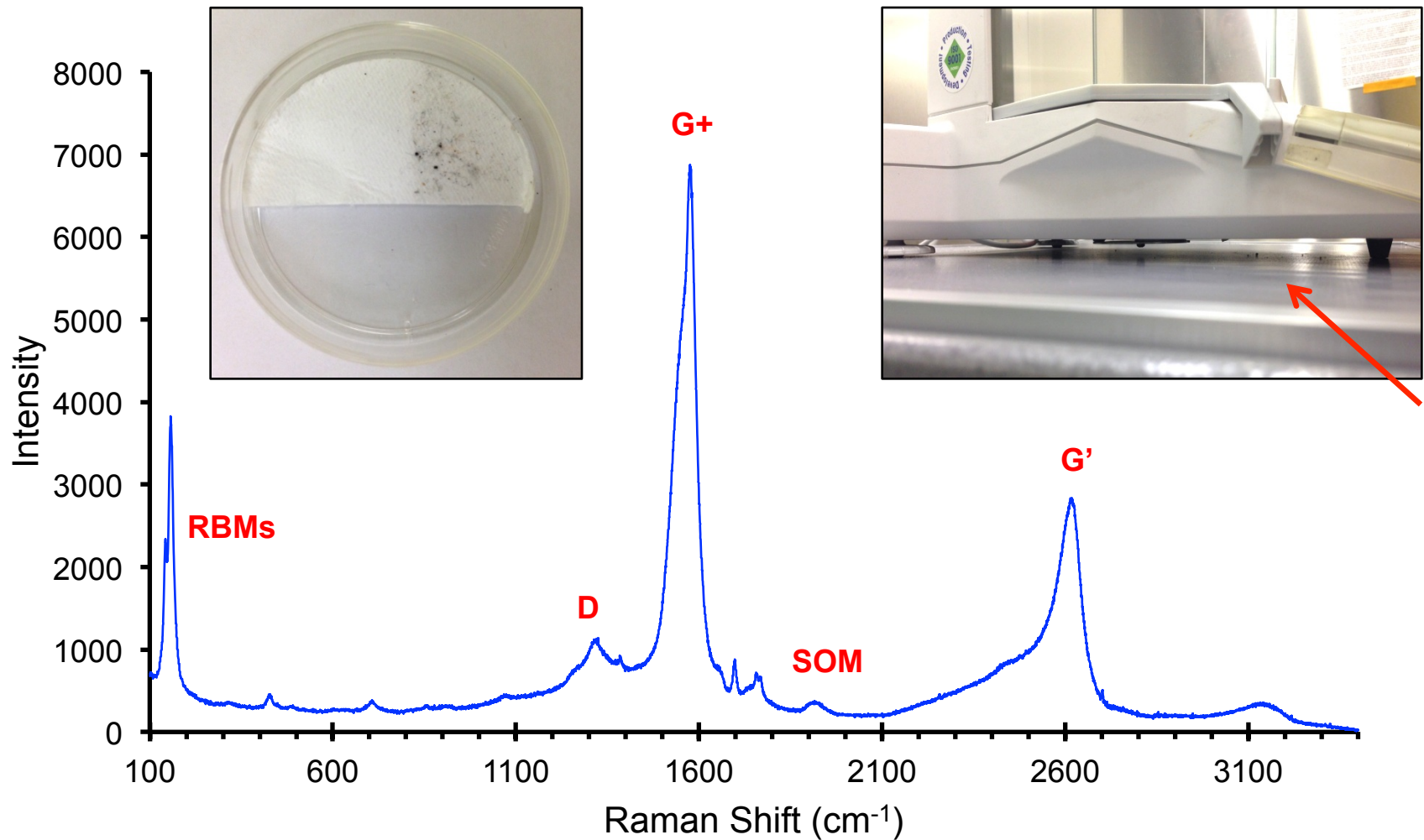


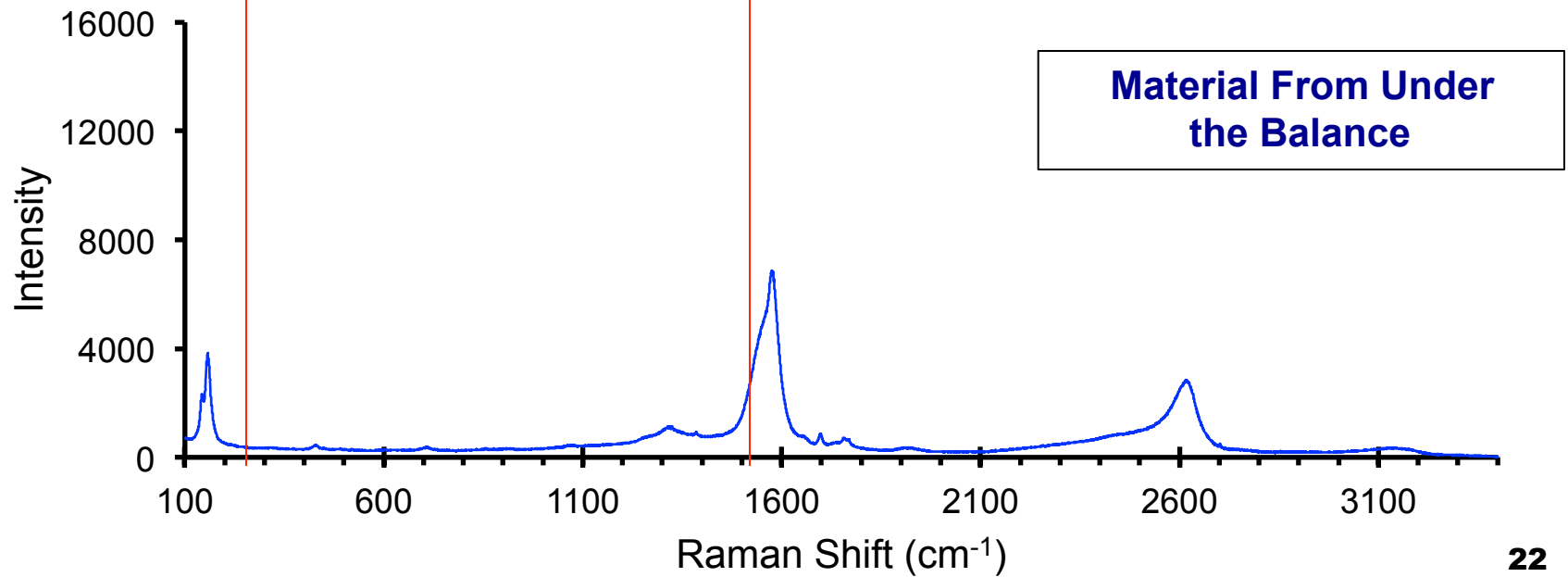
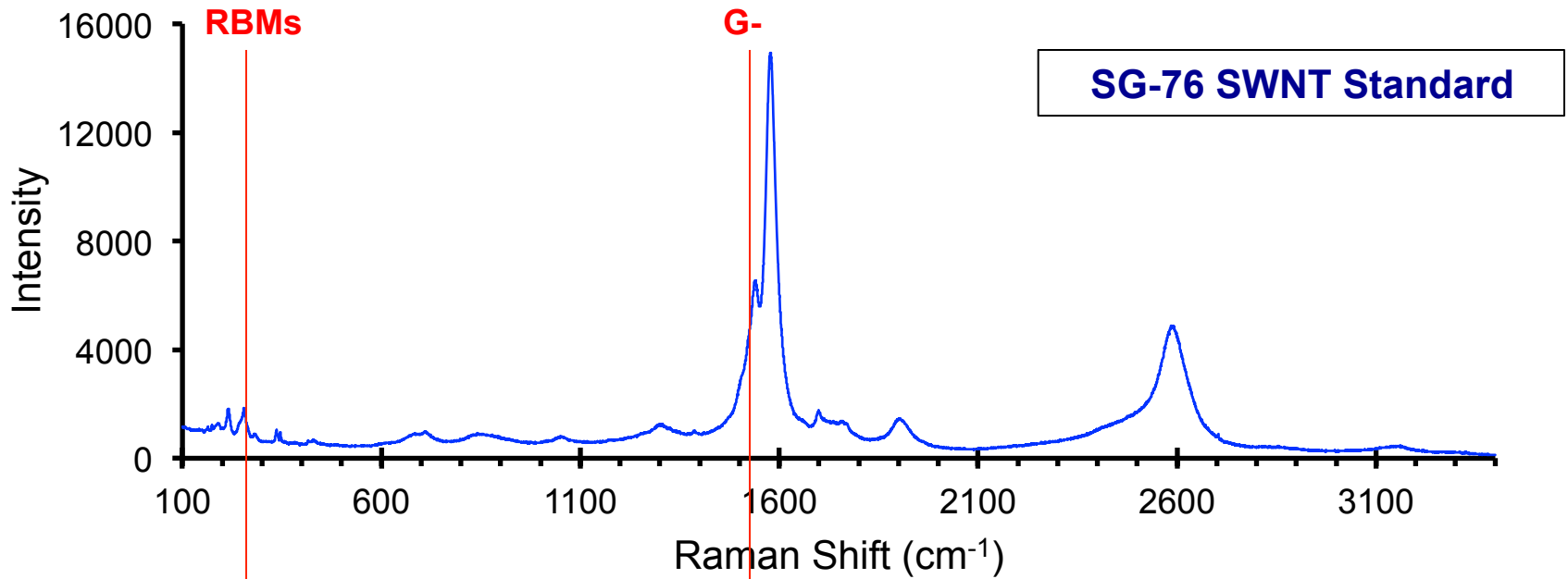
Carbon Nanotubes or Particulate Matter?

Is this Method Selective Enough?

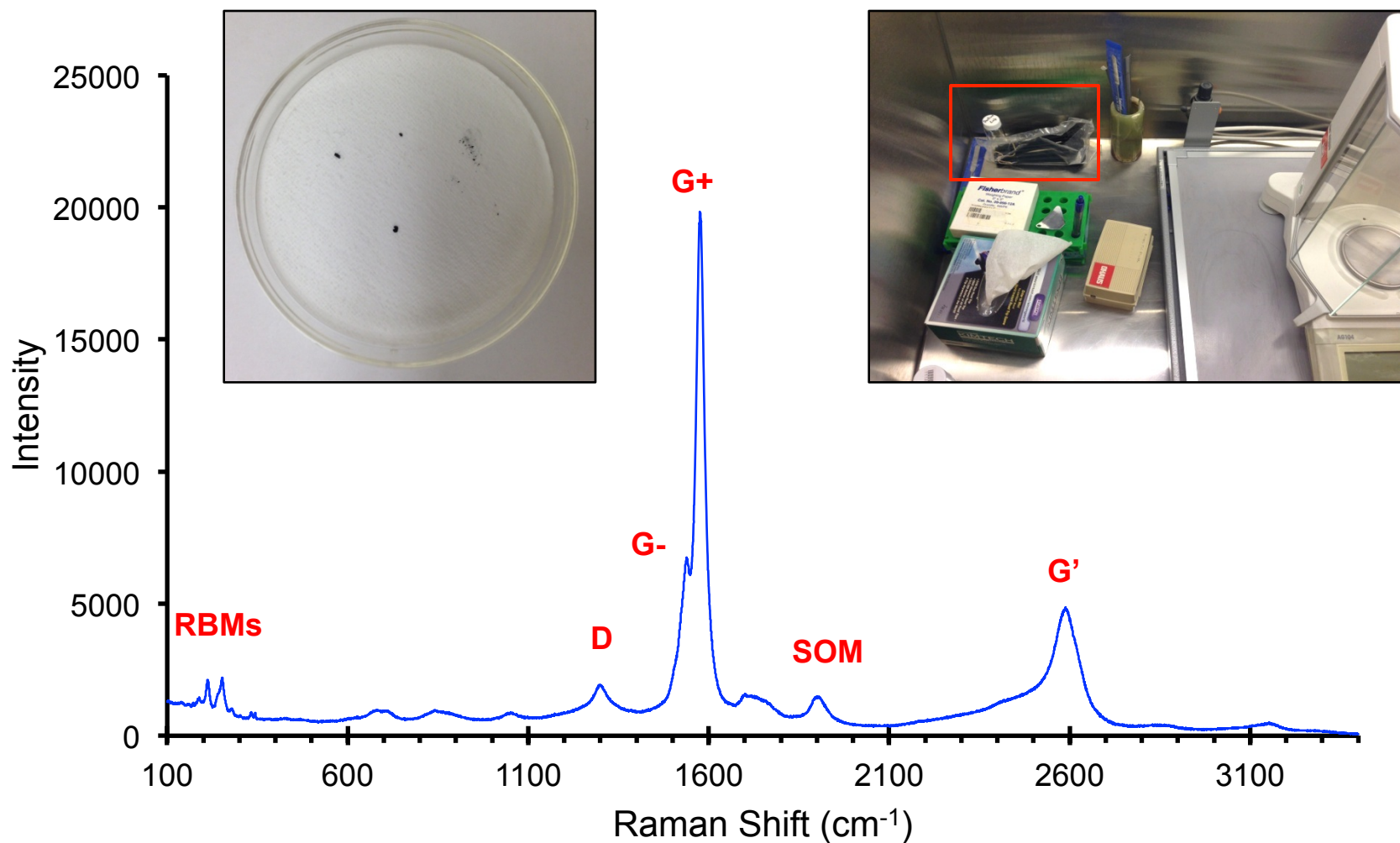


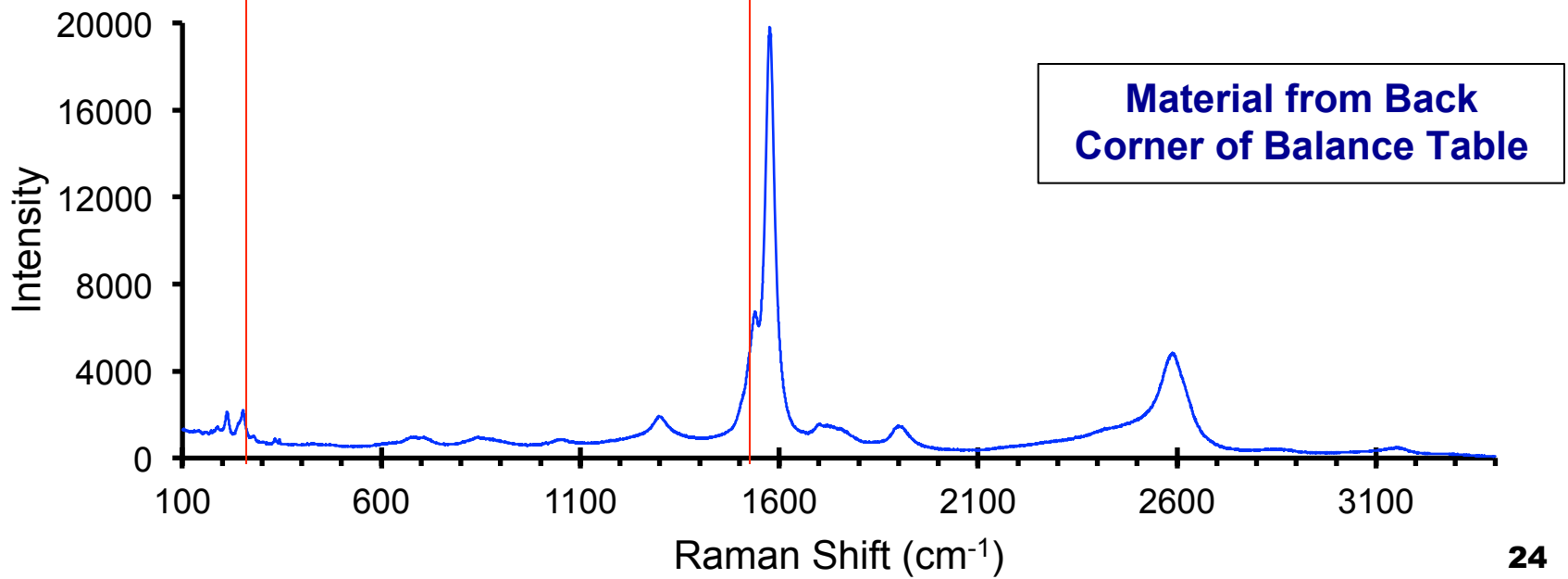
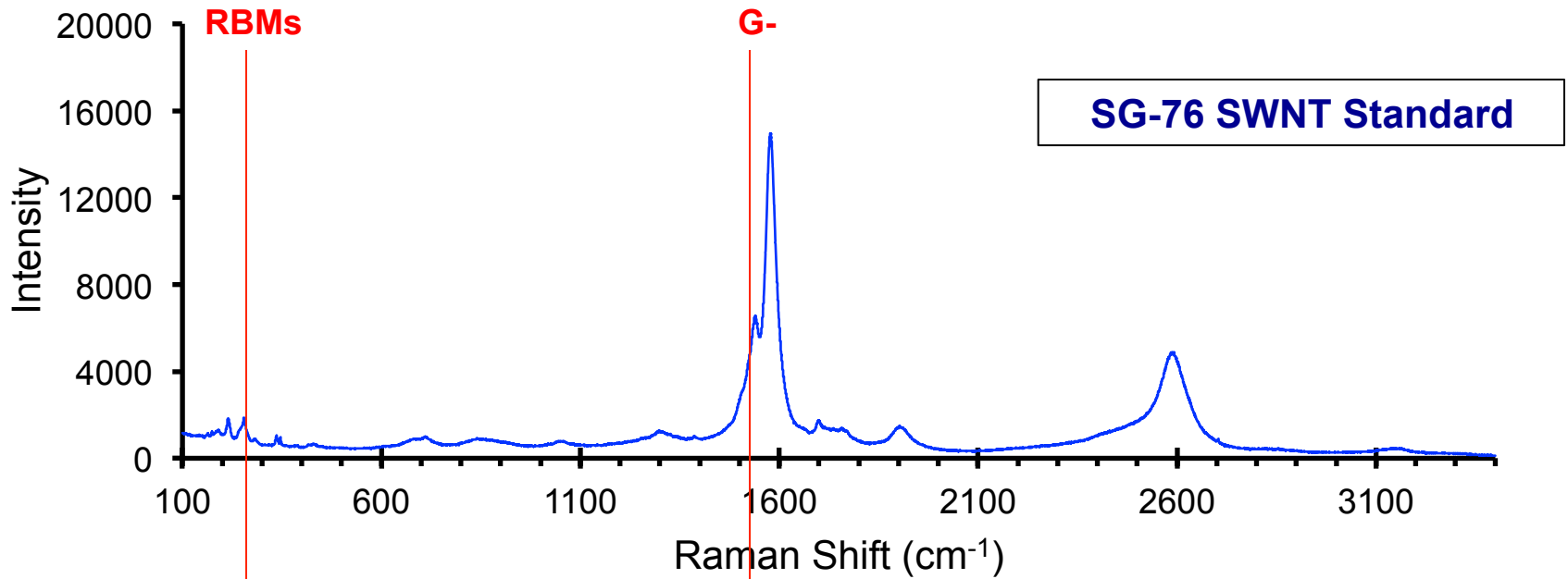
633-nm Raman Spectrum of Dark Material from Under the Balance



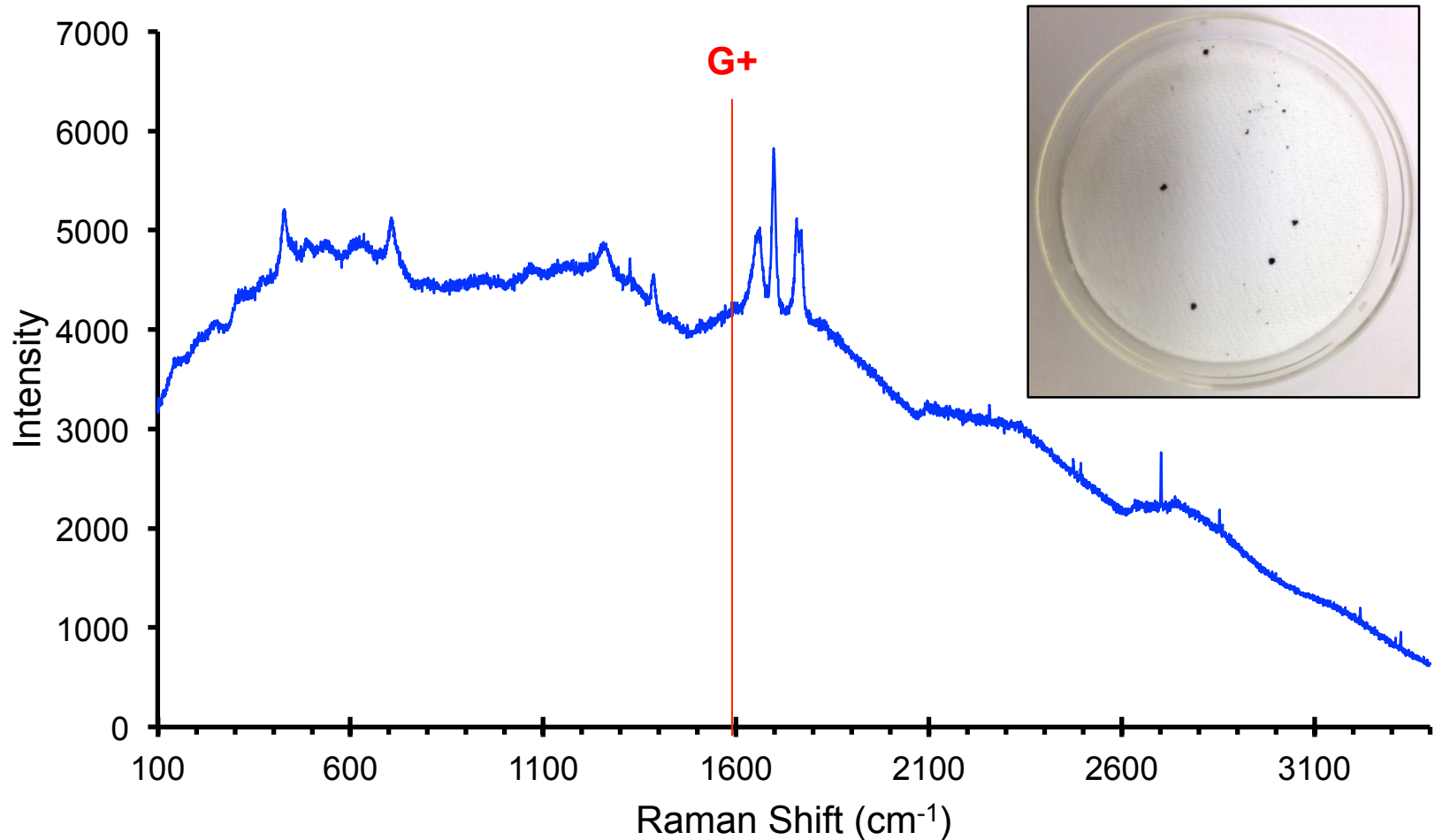


633-nm Raman Spectrum of Dark Material from Back Corner of Balance Table



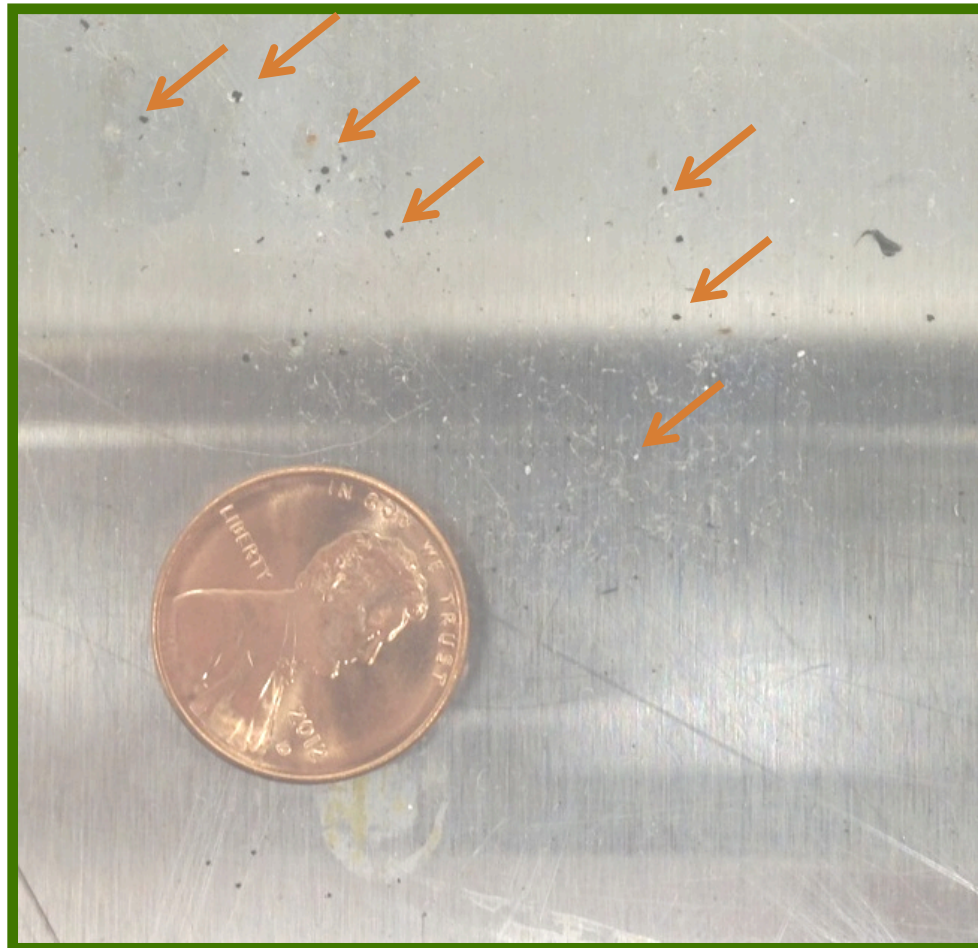


633-nm Raman Spectrum of Dark Material from a Table Across the Room



Yes, this Method is Selective

CNT Contamination Cannot be Visually Detected!



National Institute for Occupational Safety and Health (NIOSH) Recommendation

**1 $\mu\text{g}/\text{m}^3$ elemental carbon as a respirable mass
8-hour time weighted average concentration**

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

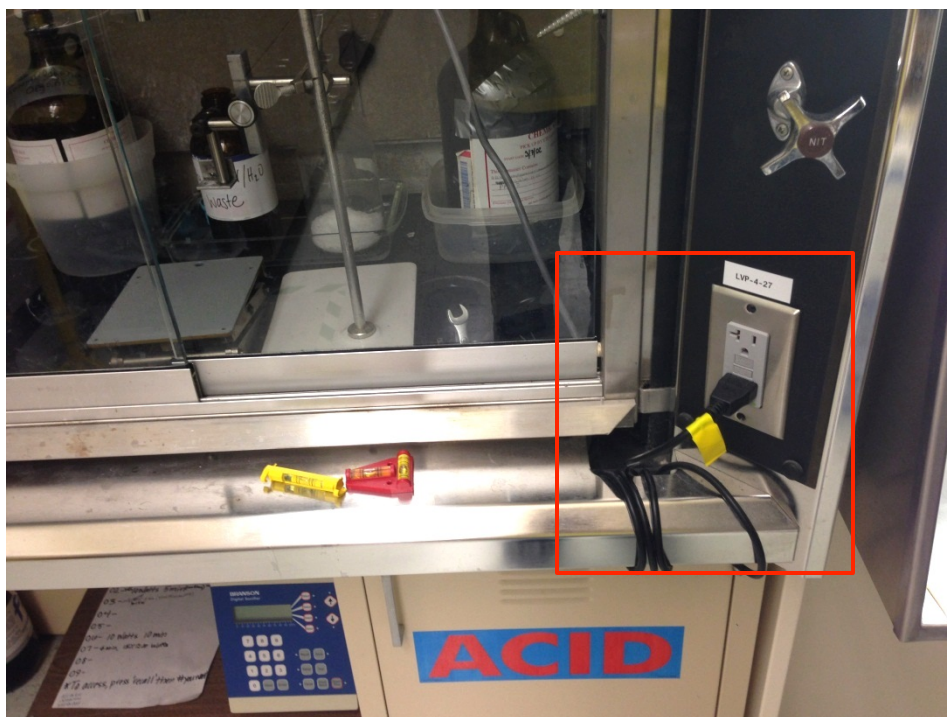
Why is this a recommendation and not a regulation?

- **Conflicting reports in literature about CNT toxicity.**
 - [Warheit DB, Toxicol Sci. vol. 77, issue 1 (2004) 117-125]
 - [Lam CW, Toxicol Sci. vol. 77, issue 1 (2004) 126-134]
- **There is a lack of contamination data from laboratories or worksites in which nanomaterials are handled.**

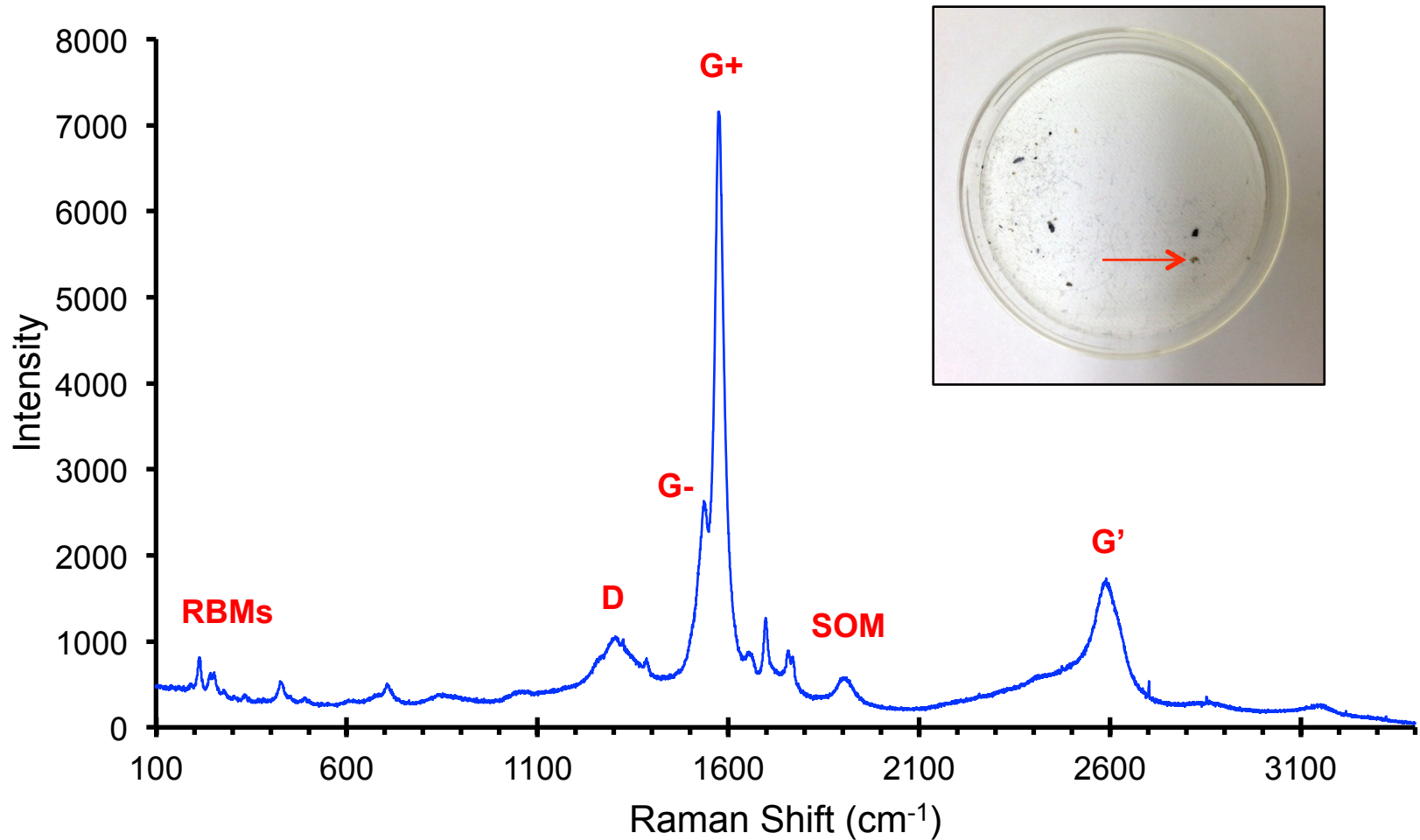
How Widespread is the CNT Contamination?

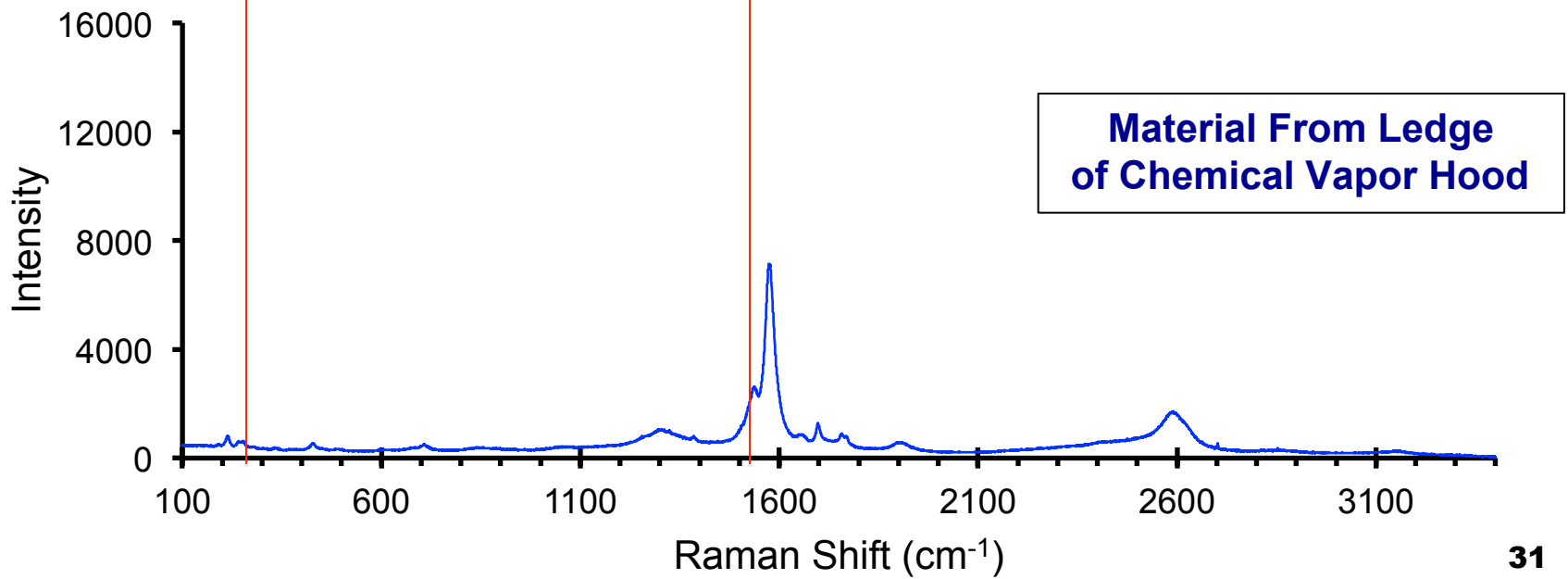
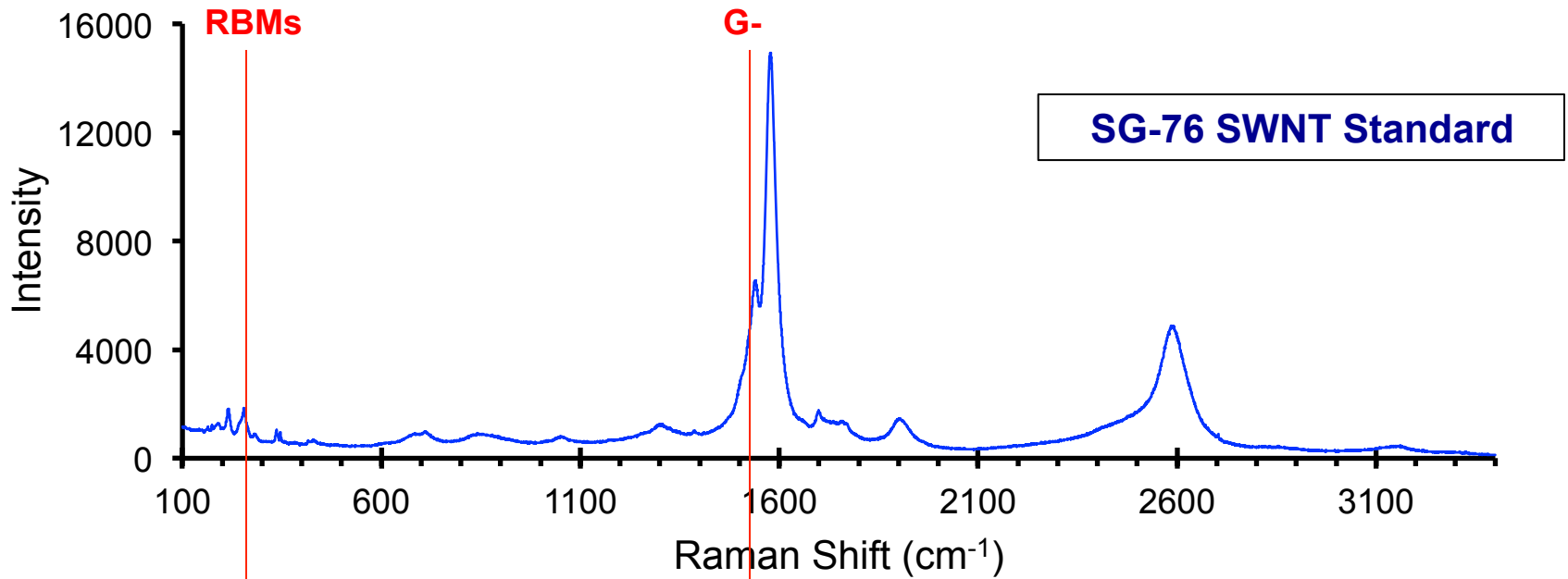


How Widespread is the CNT Contamination?



How Widespread is the CNT Contamination?





Conclusions

- μg amounts of SWNTs were detected on workplace surfaces

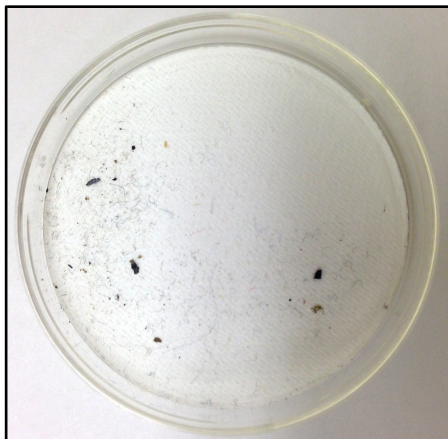
(Note: Air sampling tests have not been performed.)



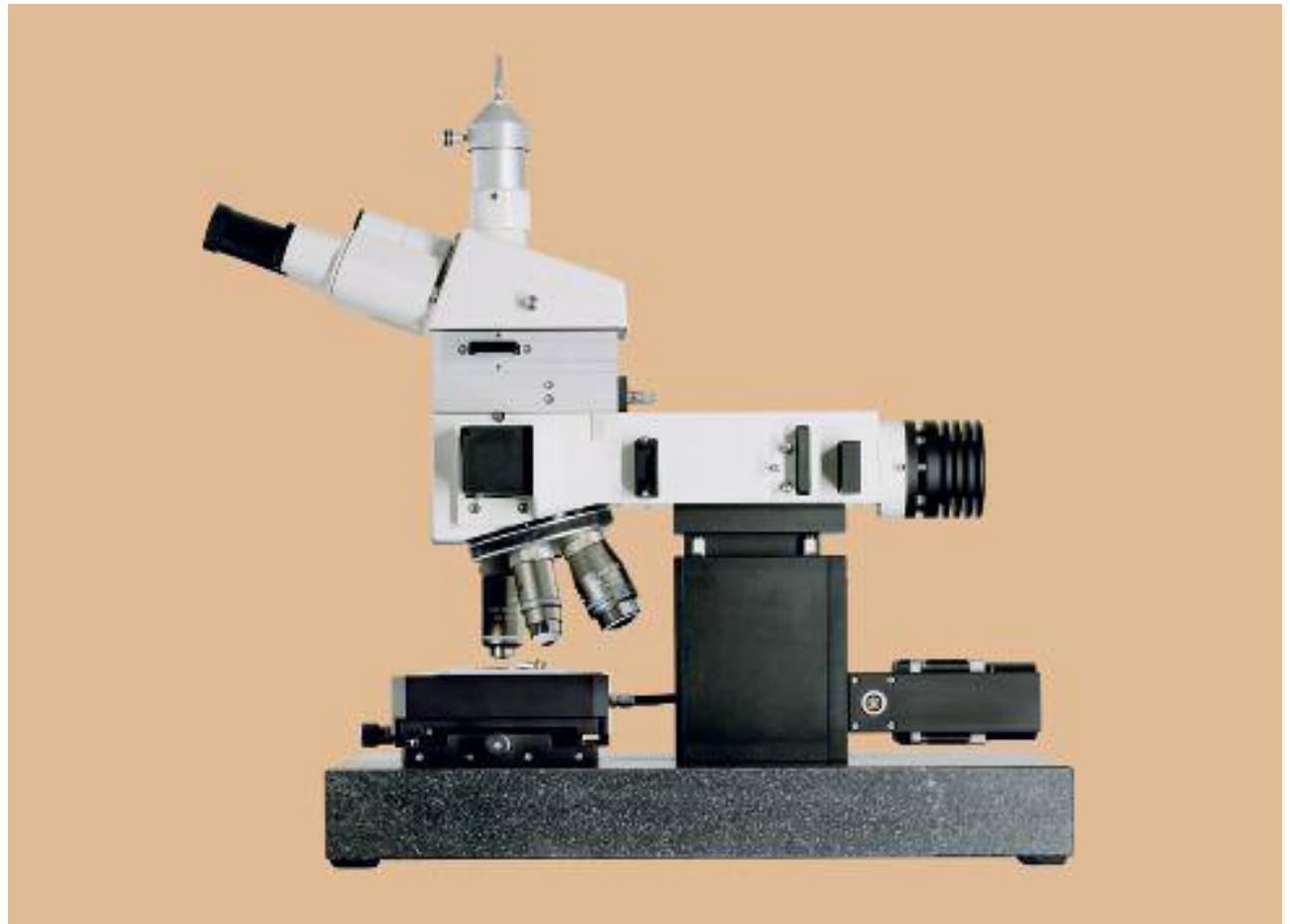
- Graphene, Graphene Oxide, and MWNT Users 😊

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



WITec
focus innovations
*Raman Spectral
Imaging*



alpha 300R scanning confocal Raman microscope
with 532-nm and 785-nm laser excitation



www.utd.edu/~pantano

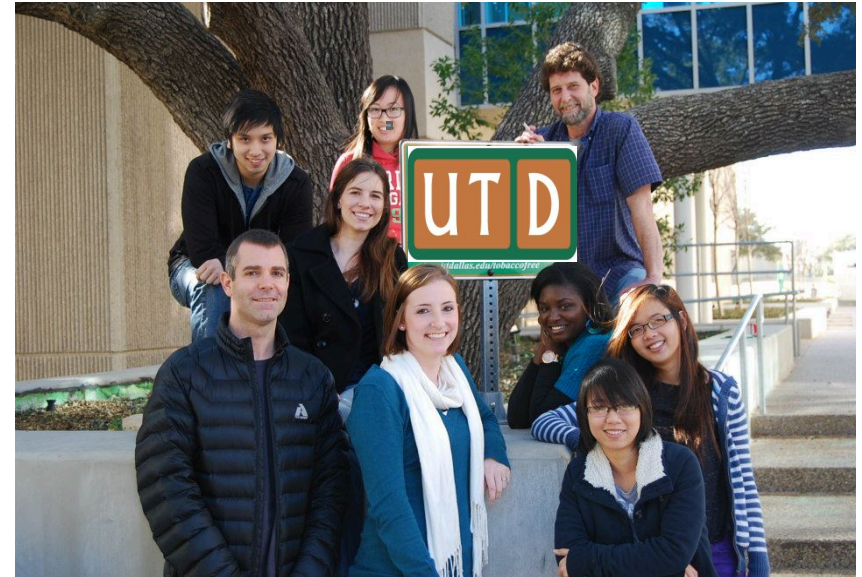


PantanoLABO

est. 1996

Paul Pantano
Elizabeth Braun
Winston Layne

ERC Task 425-042



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