Carbon Nanotube and Graphene Quantification

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SRC TeleSeminar

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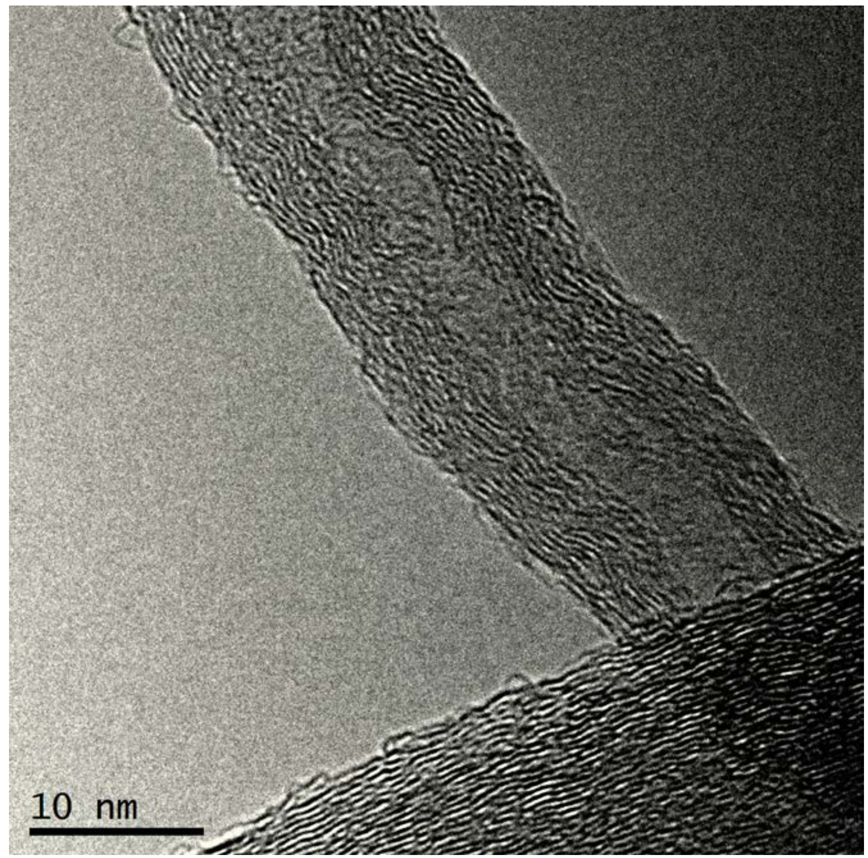

Current Methods Available

- Thermogravimetric analysis
  - Only accounts for weight change
- Radiolabeling
  - Must be pre-labled
  - Very sensitive
- Fluorescence
  - Only valid for semiconducting SWCNTs
- Electrophoresis
  - Sensitive
  - Anything dark in color may interfere
  - Not all CNTs will stay at gel interface
- Metal analysis (ICP)
  - Only valid for CNTs containing metals
  - Sensitive

Method Development

Environmental Science & Technology
Article
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Detection of Carbon Nanotubes in Environmental Matrices Using Programmed Thermal Analysis

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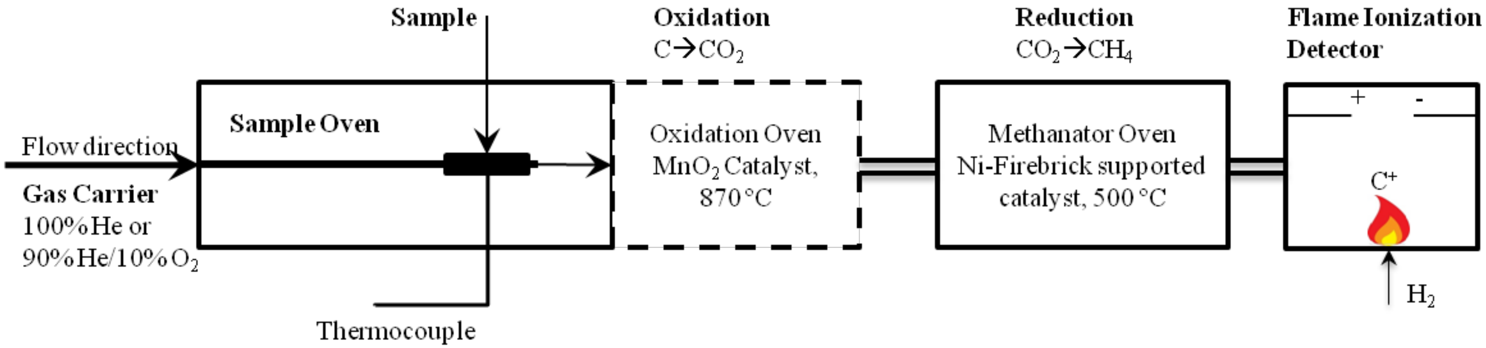
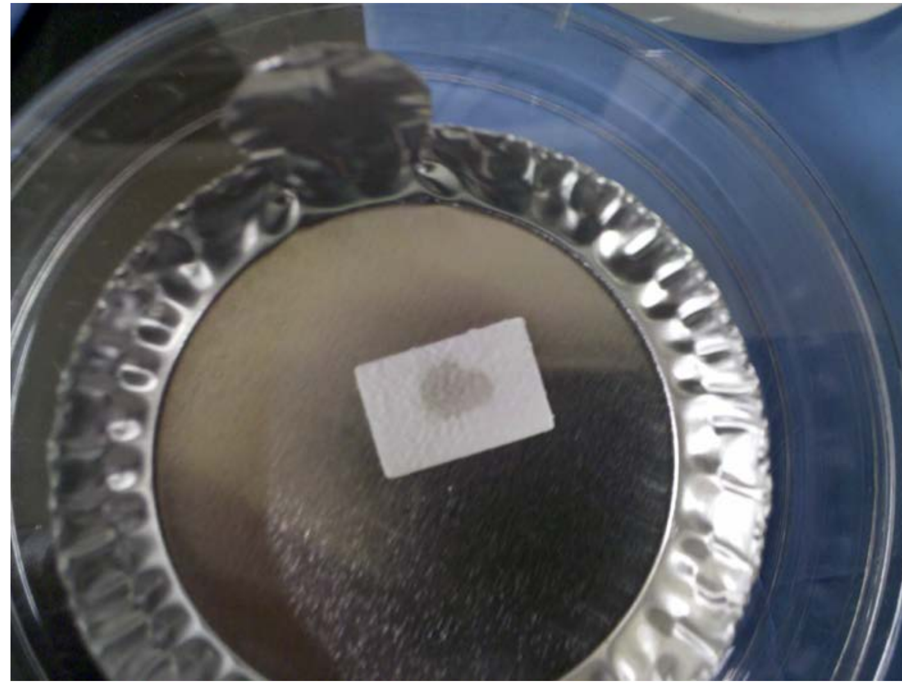
Doudrick, K., P. Herckes, P. Westerhoff. Detection of carbon nanotubes in environmental matrices using programmed thermal analysis. *Environ. Sci. Technol.*, 46(22), 12246–12253, 2012.

Instrument used to developed analytical method

- Sunset Laboratory (Forest Grove, OR) Thermal Optical Transmittance
- Traditionally used to measure soot in air using NIOSH standards (Method 5040B) and also organic (OC) and elemental carbon (EC) in air pollution studies



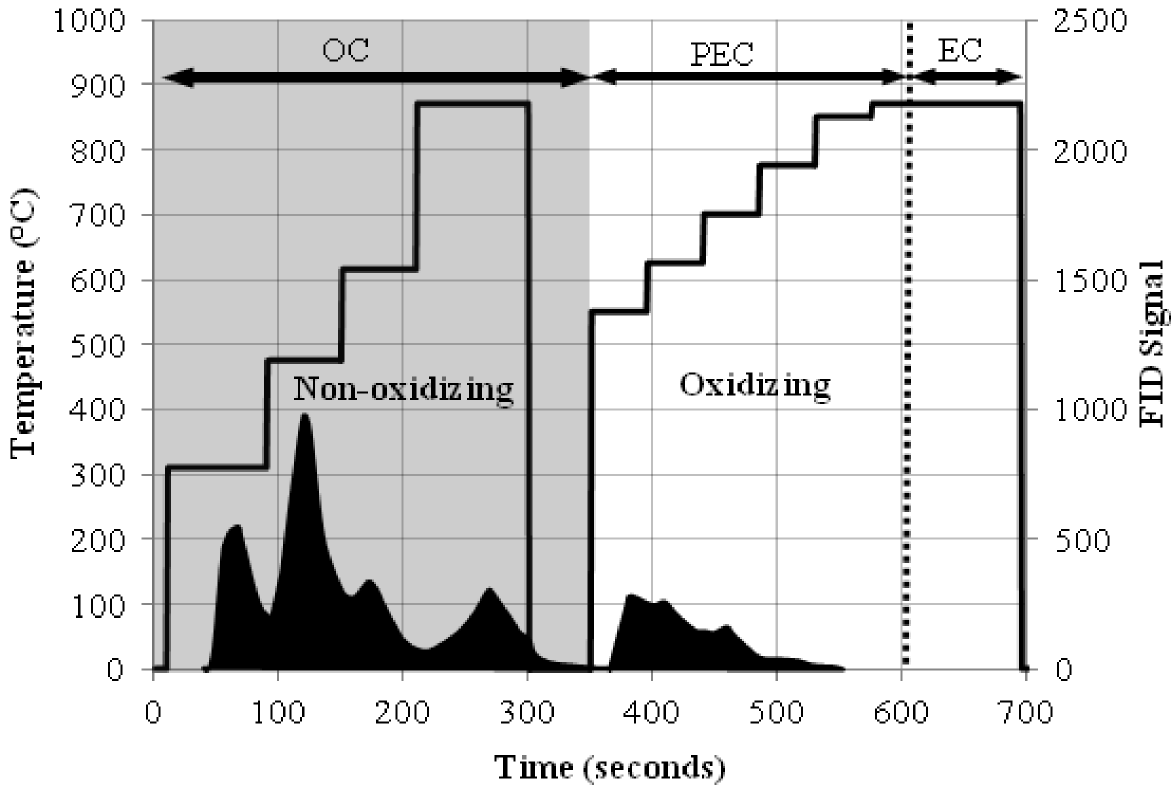
Sample Filters



Sample Holder

Thermogram and carbon definitions

Sucrose

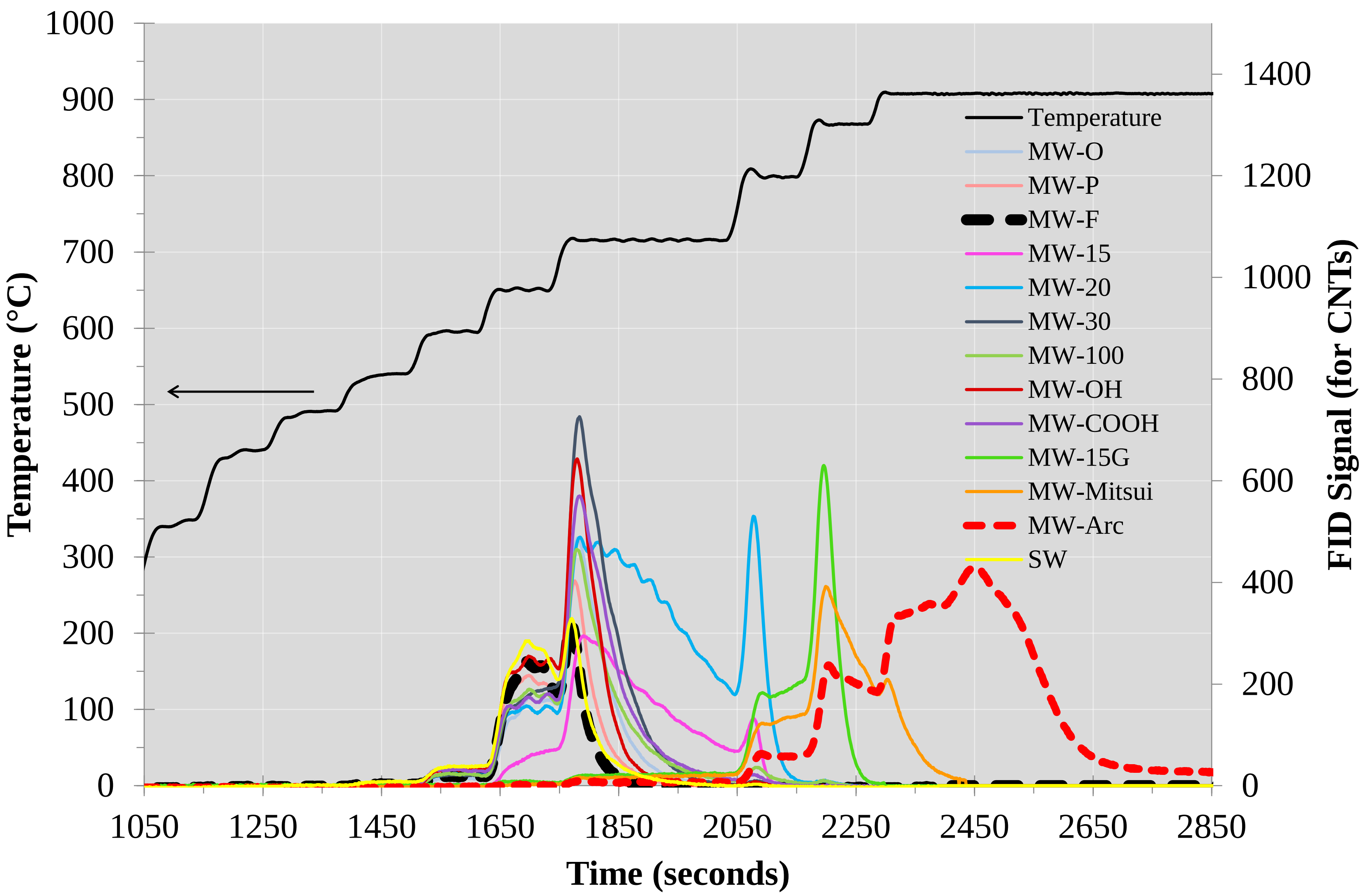


CNT Characterization

CNT ID	CNT Type	State	Purity[a]	Metal Content[b]	Outer Diameter (nm)	Inner Diameter (nm)	Length (µm)
MW-O	MWCNT	Raw	>95%	<6%	20-30	5-10	10-30
MW-P	MWCNT	Purified	>98%	<2%	20-30	5-10	10-30
MW-F	MWCNT	Functionalized	>99.9%	<0.01%	20-30	5-10	10-30
MW-15	MWCNT	Raw	>95%	<5%	7-15	3-6	0.5-200
MW-20	MWCNT	Raw	>95%	<5%	10-20	5-10	0.5-200
MW-30	MWCNT	Raw	>95%	<5%	10-30	5-10	0.5-500
MW-100	MWCNT	Raw	>95%	<5%	60-100	5-10	0.5-500
MW-OH	MWCNT	Functionalized	>95%	<1.5%	8-15	3-5	10-50
MW-COOH	MWCNT	Functionalized	>95%	<1.5%	8-15	3-5	10-50
MW-15G[c]	MWCNT	Annealed	>97%	<1%	7-15	3-6	0.5-200
MW-Mitsui	MWCNT	Raw	>98%	<1%	20-70	NA	NA
MW-Arc	MWCNT[d]	Raw	<50%	0%	5-10[e]	NA	NA
SW	SWCNT	Raw	<50%	<10%	1.1	NA	0.5-100
SW-65	SWCNT	Purified	<75%	<10%	0.8	NA	0.45-2

[a]CNT content reported by manufacturer. MW-P and MW-F calculated assuming no amorphous carbon remaining.
[b]Metal content reported by manufacturer except for MW-F and MW-P determined using energy dispersive X-ray spectroscopy and MW-15G using thermogravimetric analysis.
[c]MW-15 annealed at ~2000°C in UHP He.
[d]Synthesized using arc method; all others are CVD.
[e]Obtained from TEM images; all others reported by manufacturer.

CNT Thermograms

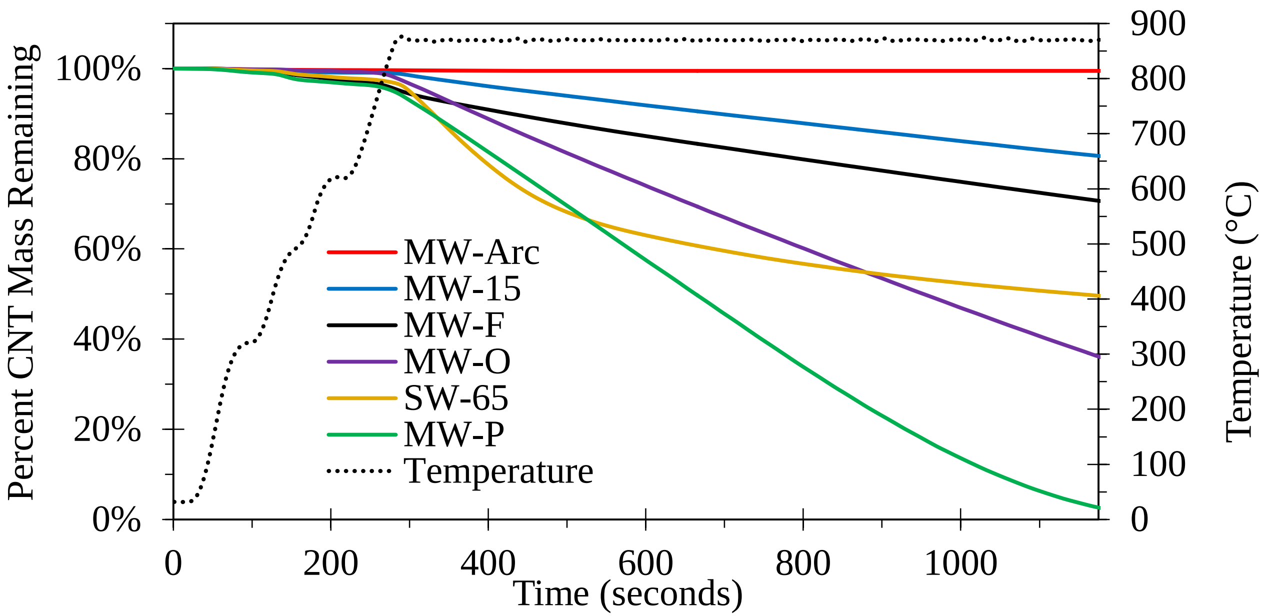


Method Development

Inert Conditions

Using NIOSH 5040B method, some CNTs desorb/oxidize at higher temperatures

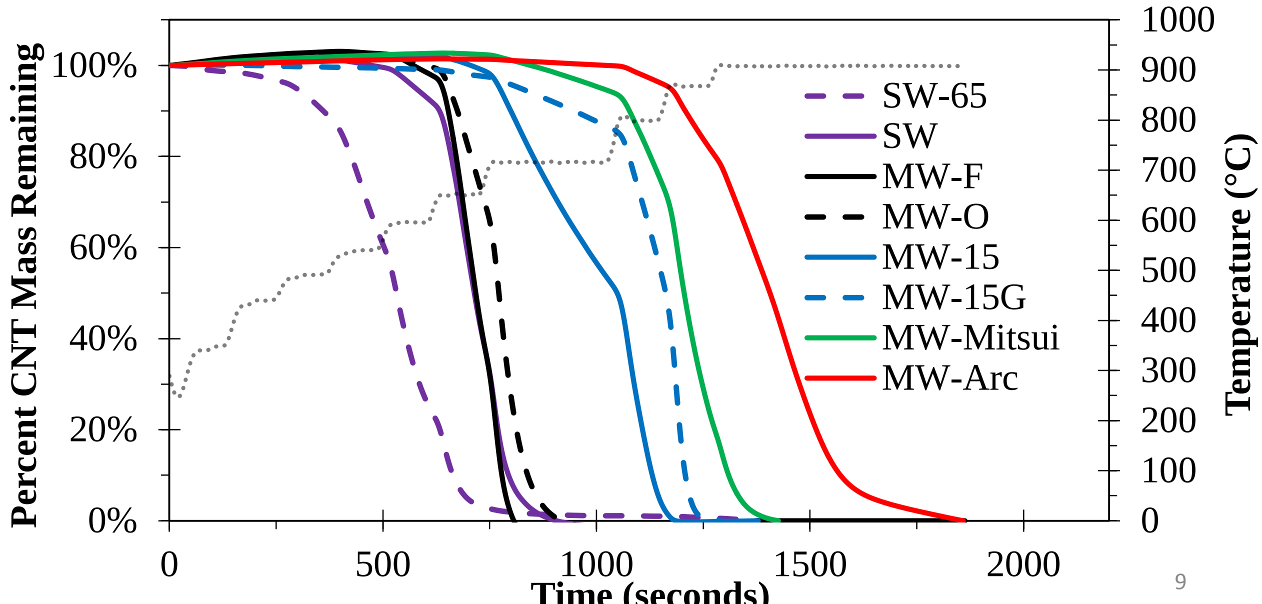
These are classified as "weak," while all that withstand higher temps are "strong"



Oxidizing Conditions

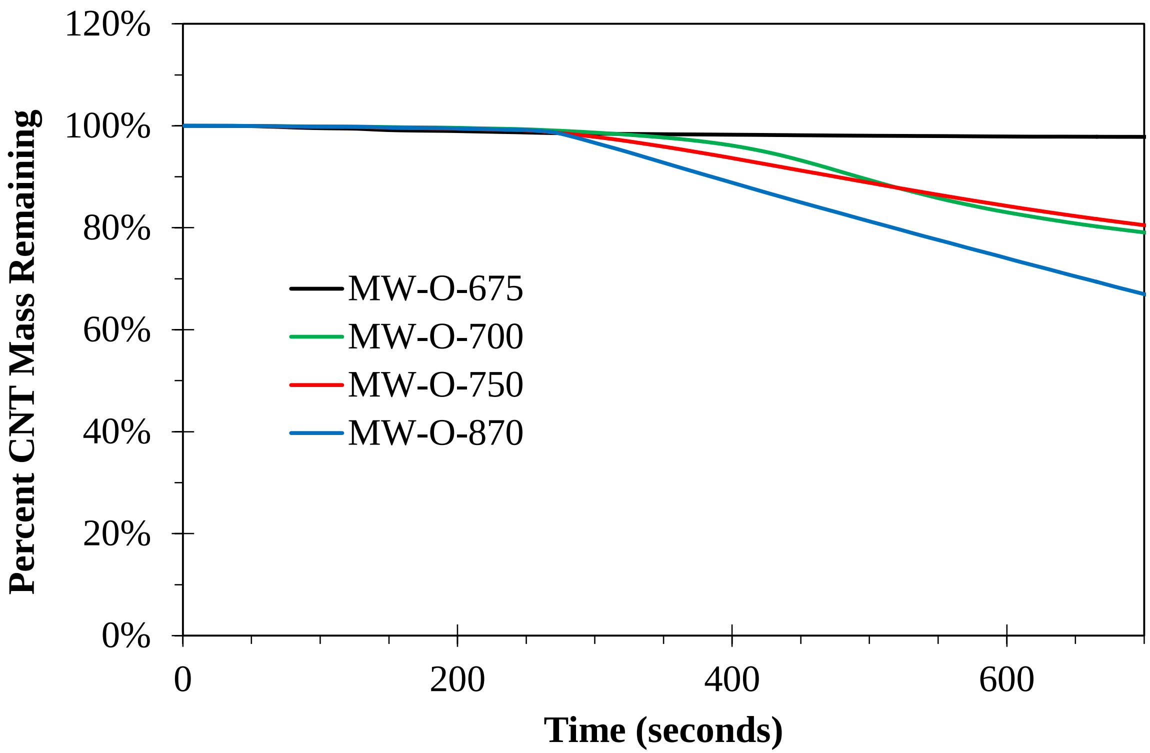
Some CNTs oxidize very early on at low temps

These are classified as "weak," while all that withstand higher temps are "strong"

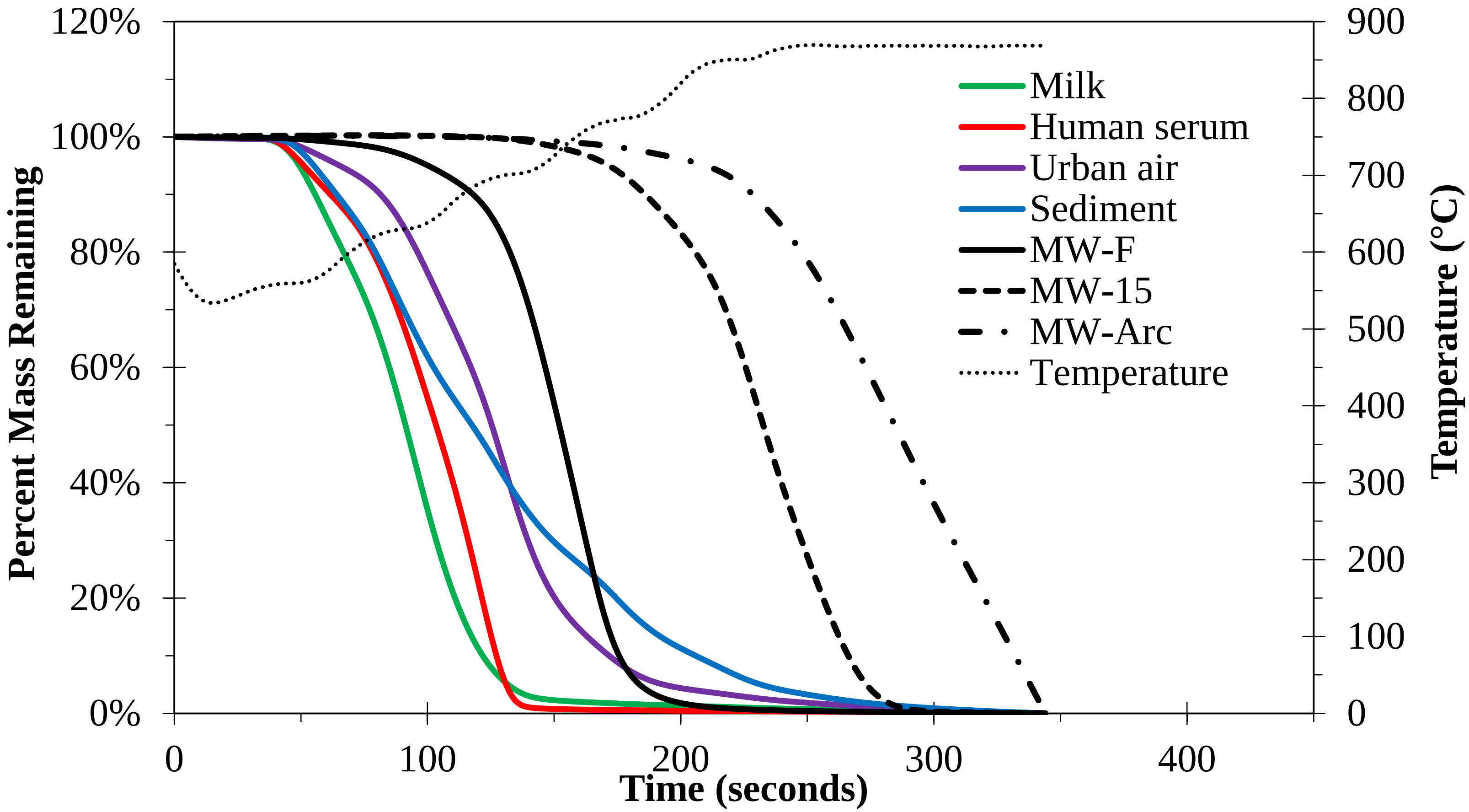


Method Development – Inert Conditions

- Examined different maximum temperature conditions for a representative weak CNT
- 675 °C was the max temp where no CNT loss occurred



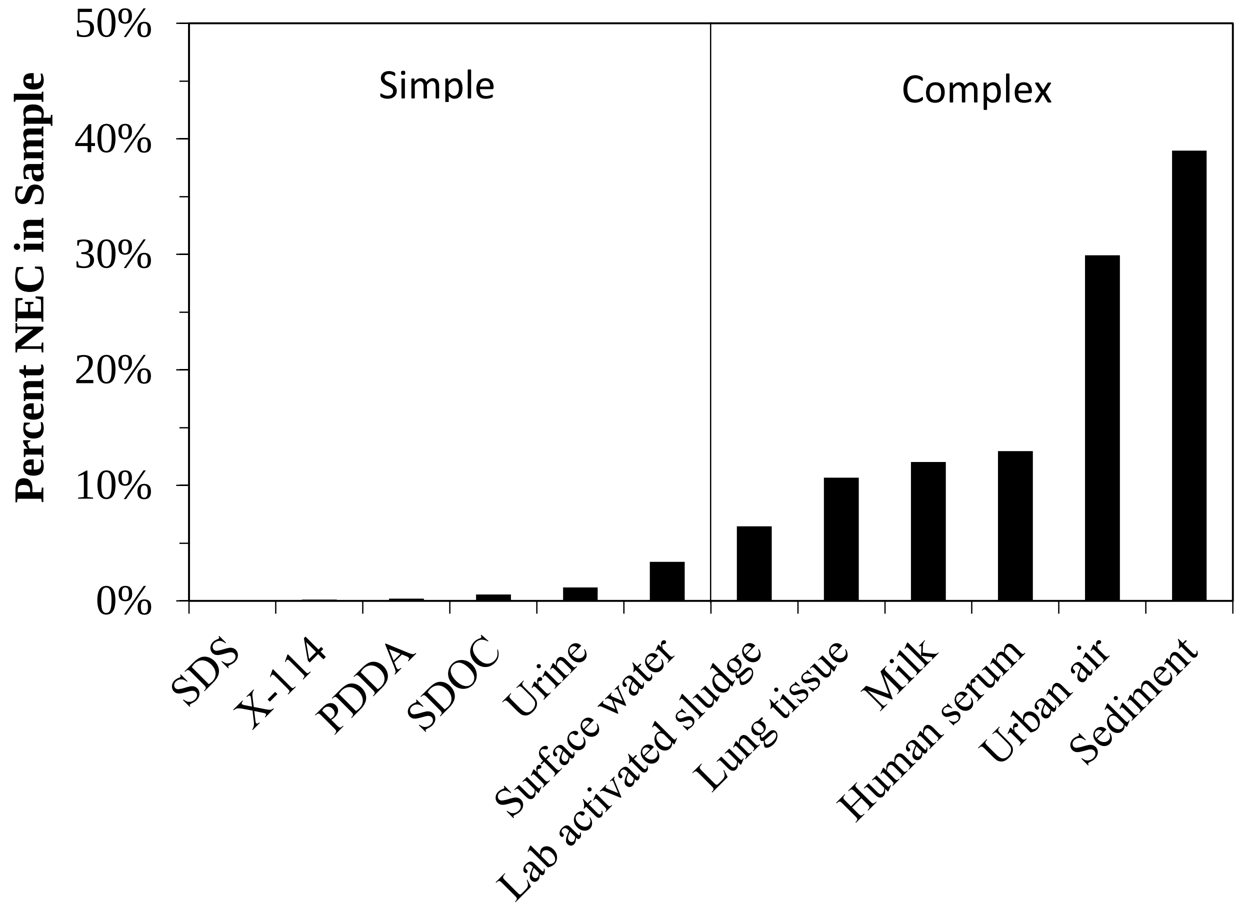
Can we measure CNTs Directly (w/o extraction)?



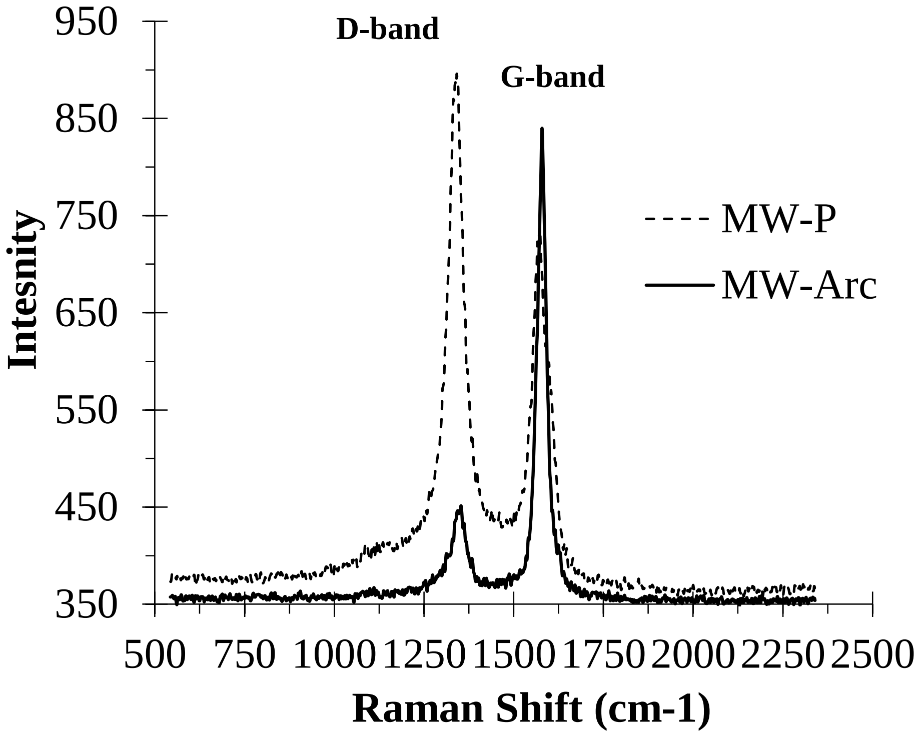
At ~95% weak CNT mass remaining, there is still 70% urban air, 60% sediment, 50% serum, and 30% milk. Sediments are the most challenging with <10% interference with even the strongest CNT

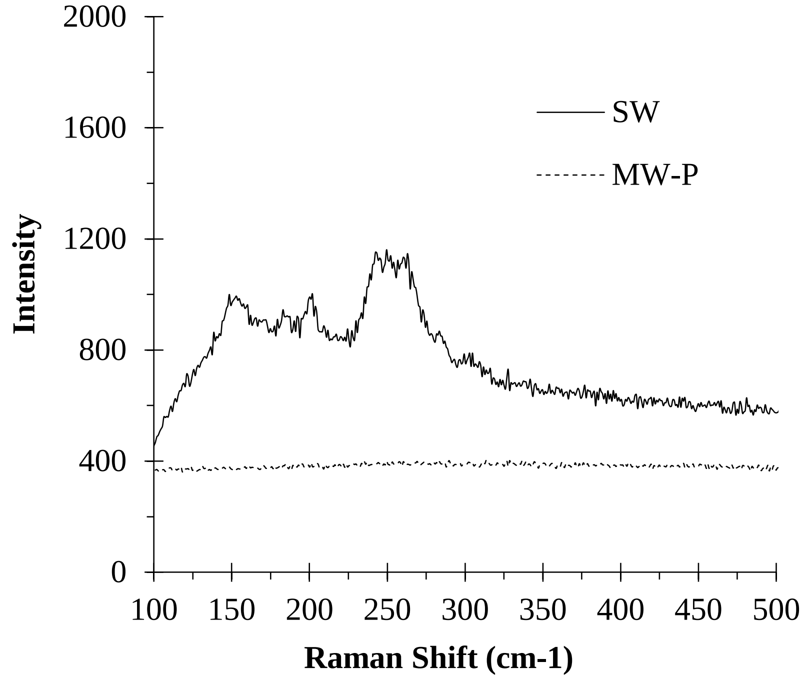
Matrix Interference

- NEC: Non-CNT Elemental Carbon (i.e., soot, PEC)
- Simple: NEC < 10%
- Complex: NEC ≥ 10%

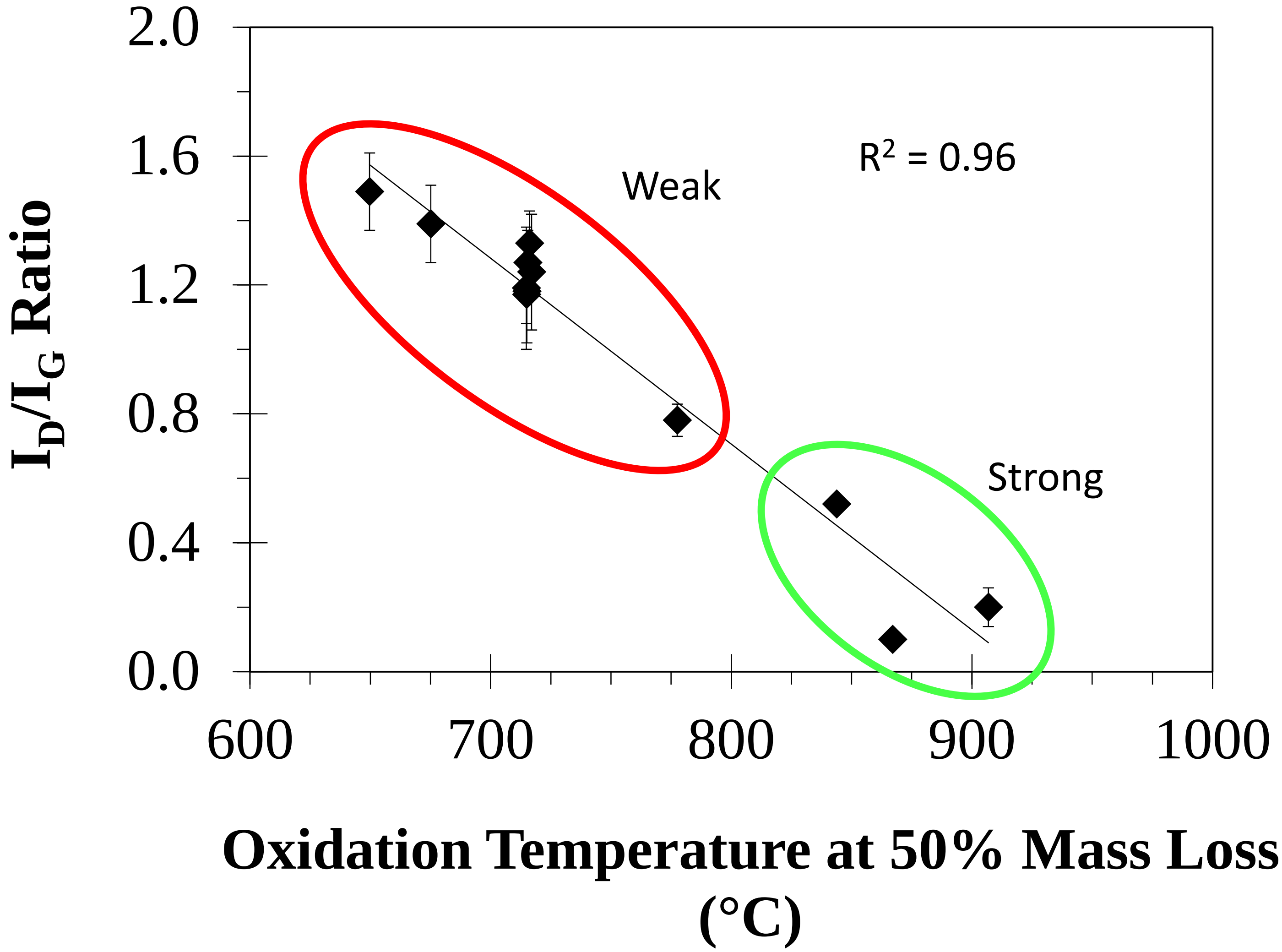


Using Raman to Determine CNT Thermal Classification





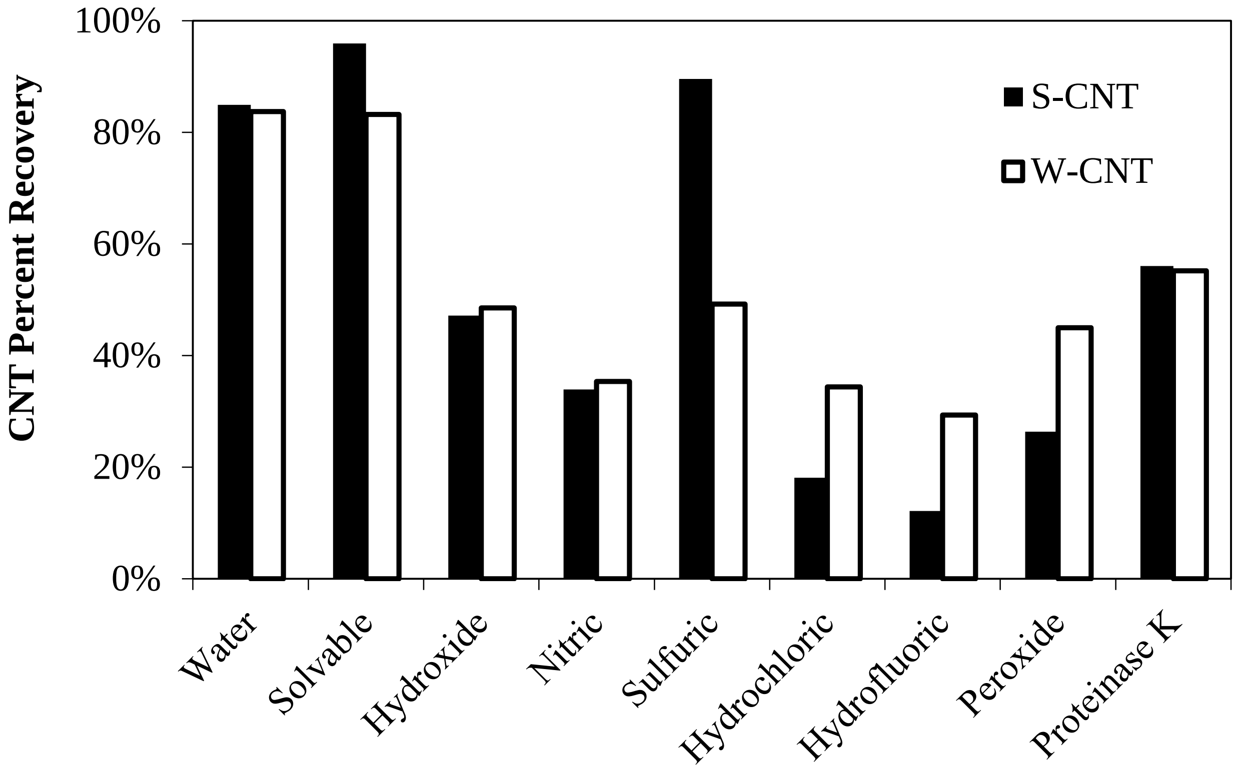
CNT Thermal Classification



Extraction

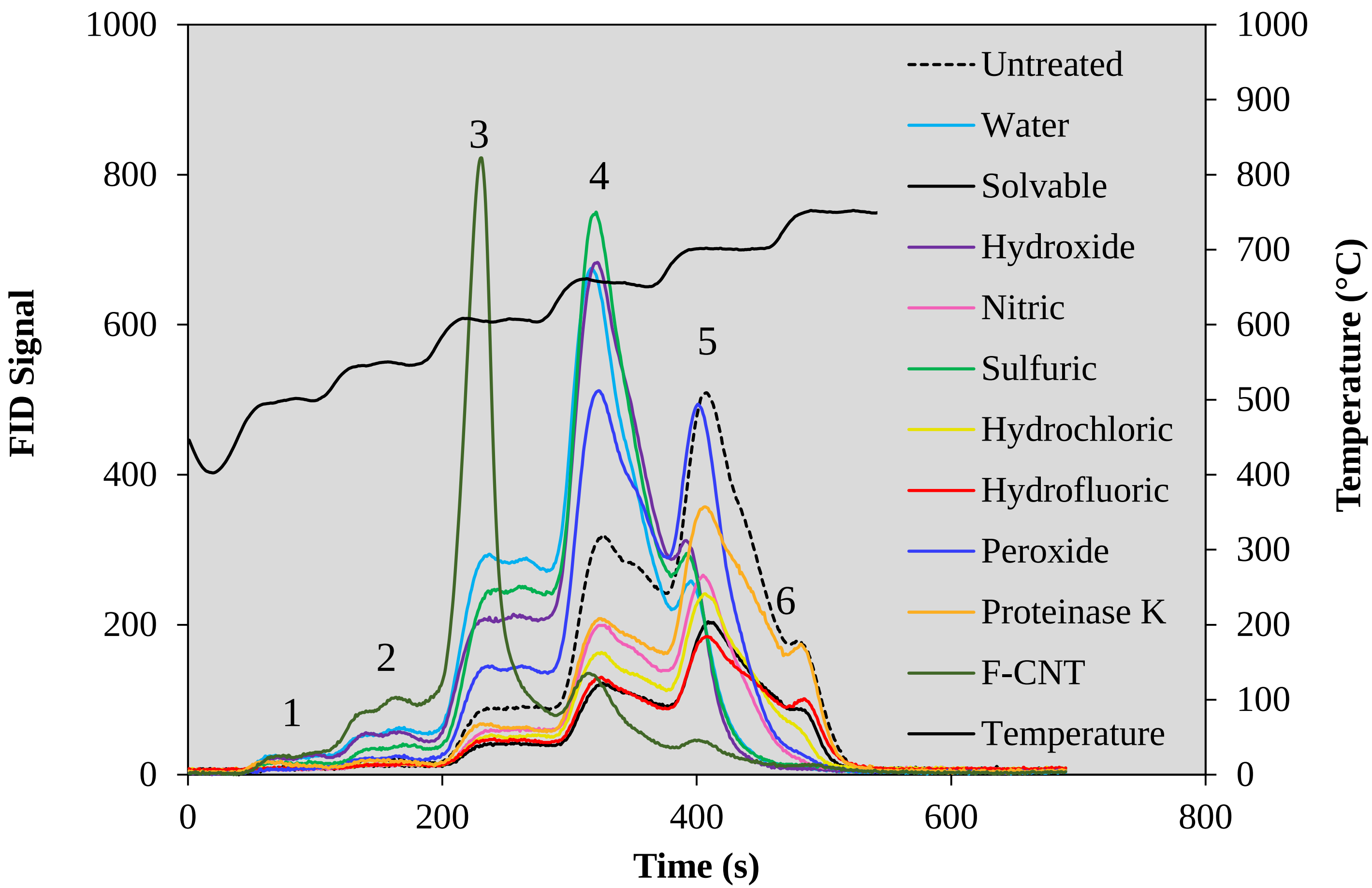
Extraction is key – CNT Recovery

- Eight different reagents (acids, alkalis, enzymes)
- 60 °C for 24 hrs with mixing
- Centrifugal separation with water washing in between
- Quantified using PTA

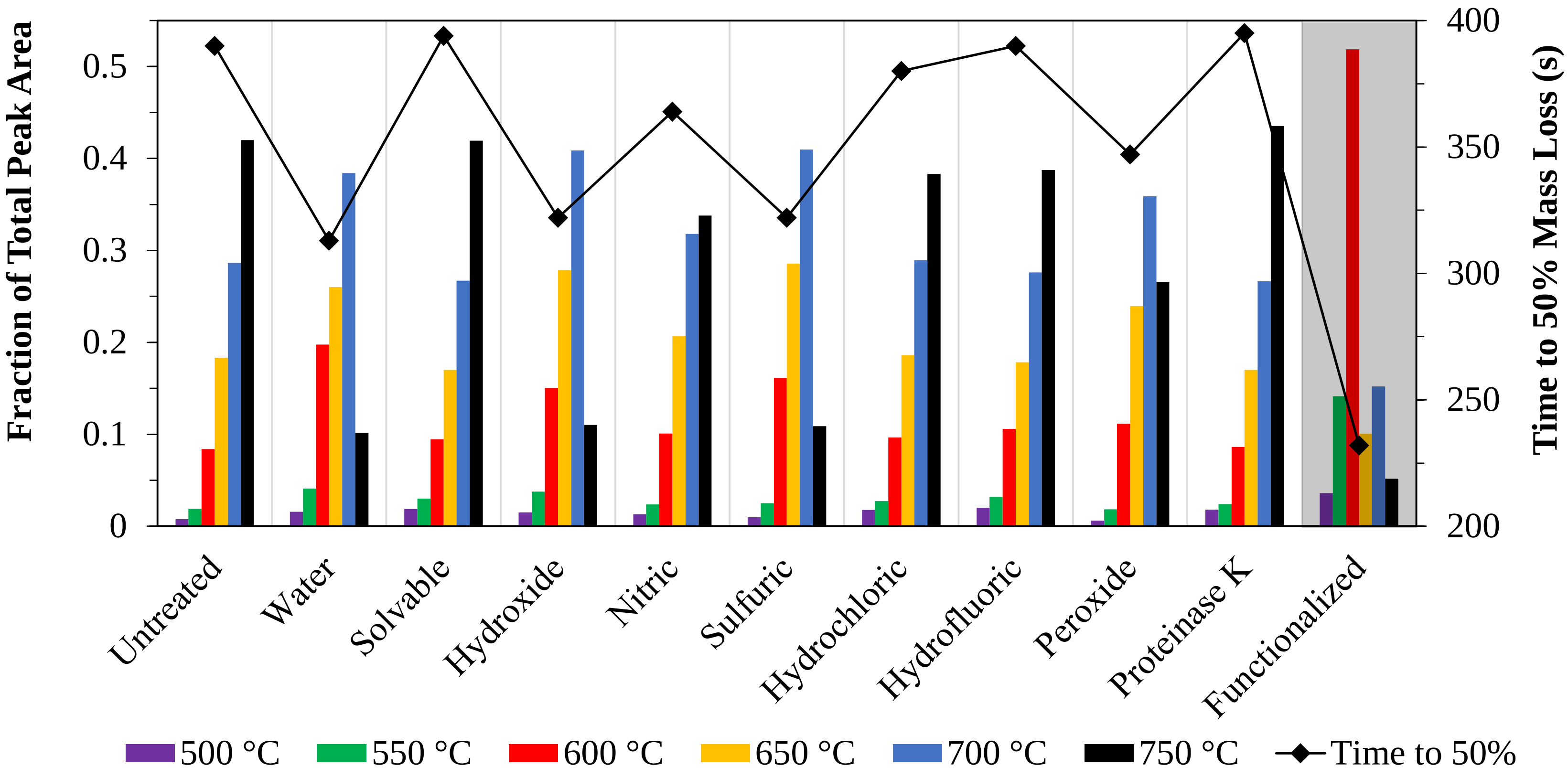


How to Compare Reagents and Analyze Damage to CNTs?

Thermograms are overly complicated!

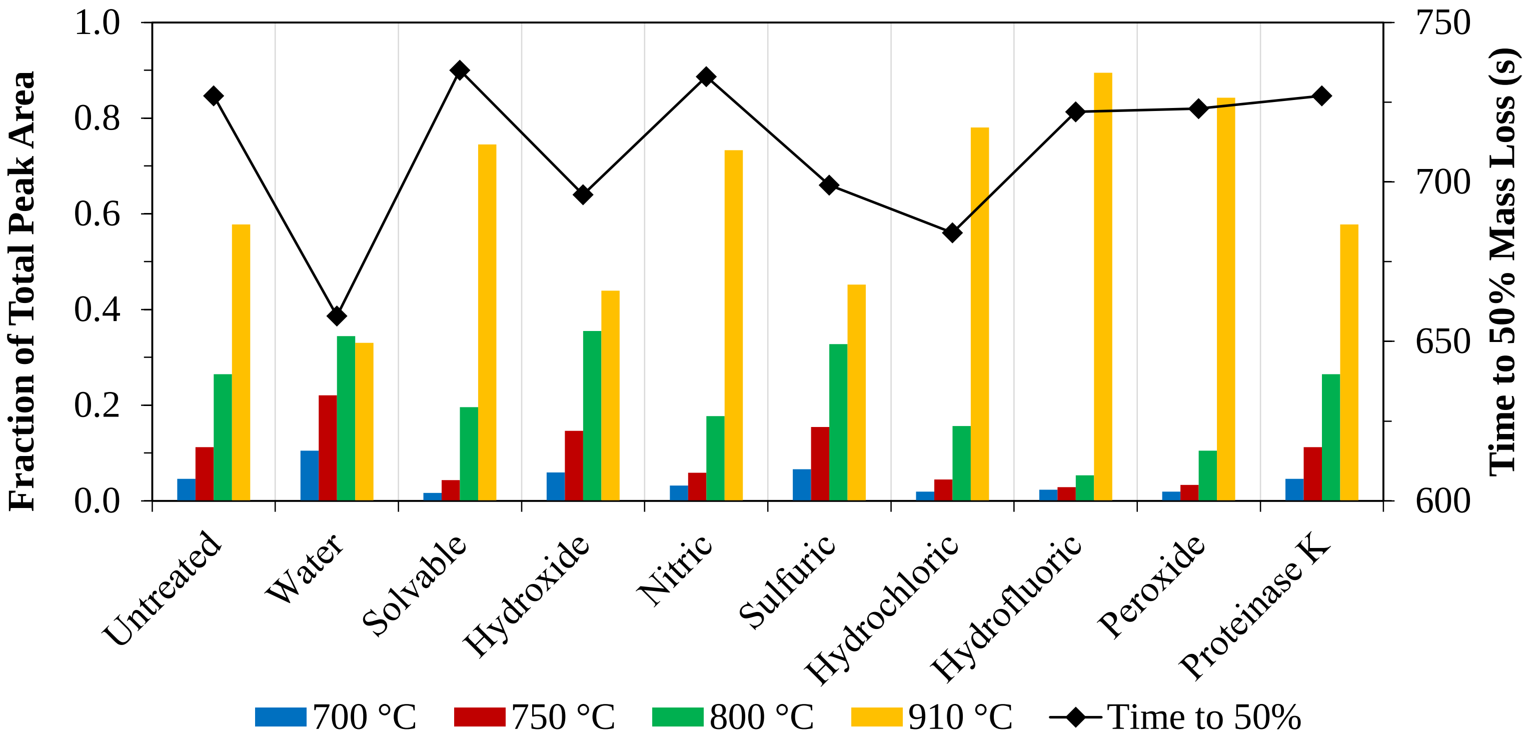


Thermogram Analysis – Weak CNTs



- Solvable, HCl, HF, and pro K showed no change (<5%)
- HNO_3 had a 5-10% change
- “Water,” NaOH, H_2O_2, and H_2SO_4 had a 10-20% change
- Functionalized CNTs had a 40% decrease

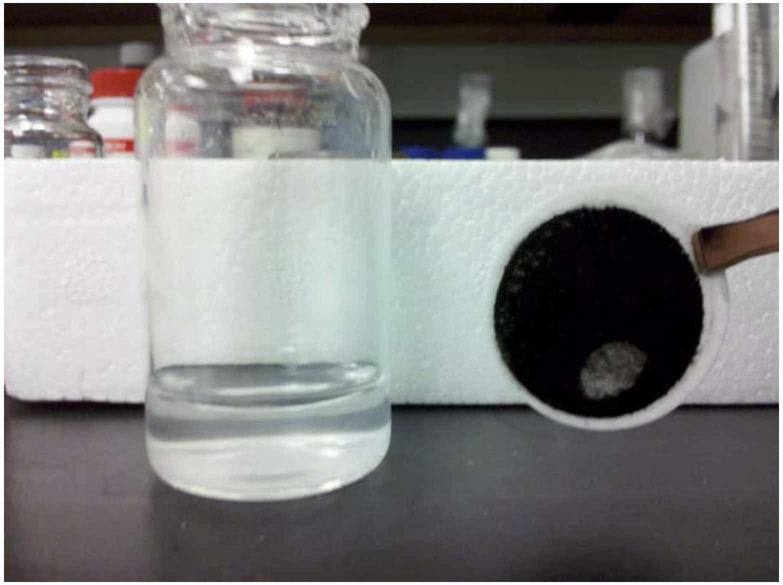
Thermogram Analysis – Strong CNTs

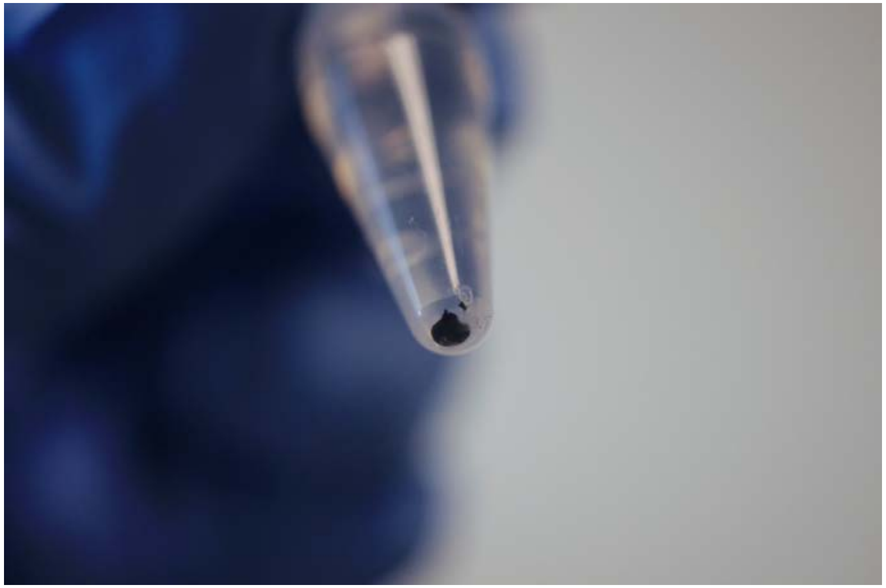


- Solvable, HF, HNO_3, H_2O_2, NaOH, and H_2SO_4, and pro K showed no change (<5%)
- "Water" and HCl had a 5-10% change

- So – HNO_3, HCl, and HF should be okay to use if separation method can be improved

Separation





- Filtration was only optimal for CNTs that were aggregated – Functionalized or fully dispersed CNTs passed partly through the filter

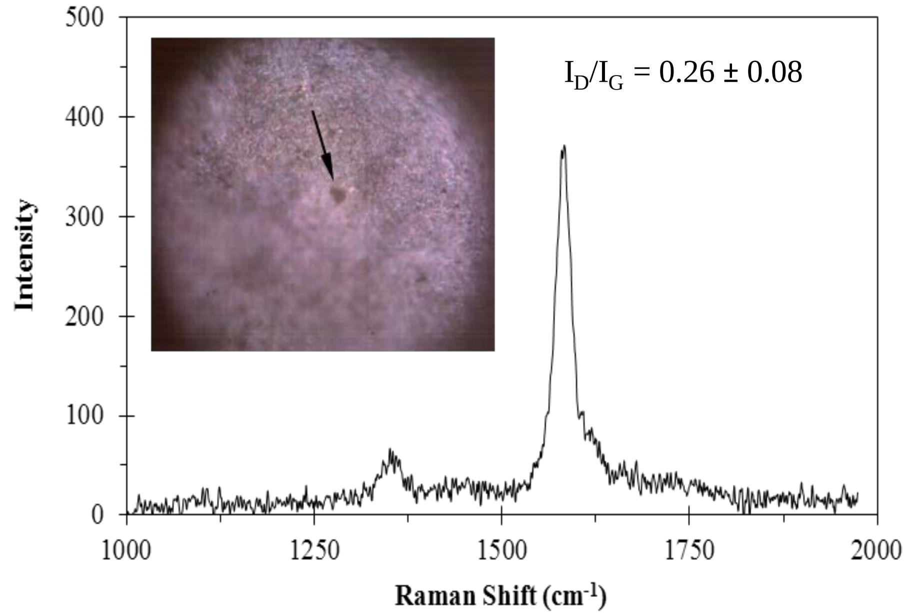
- Filtration does not allow for washing of sample to remove interferences

Reagent selection – Instrument Damage

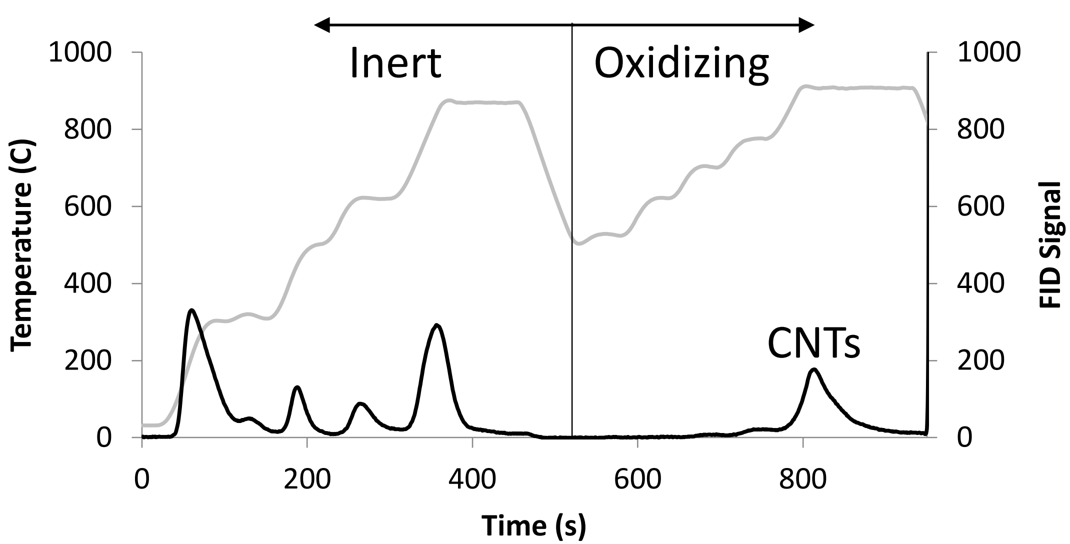
- Possibly residual acids cause corrosion
- Additional washing steps could be incorporated into method, but this may reduce recovery


Application – Cyanobacteria

- Cyanobacteria was a complex matrix and pretreatment was necessary
- Solvable or HNO_3 was adequate to dissolve CB
- Raman revealed the CNT to correctly to a strong CNT

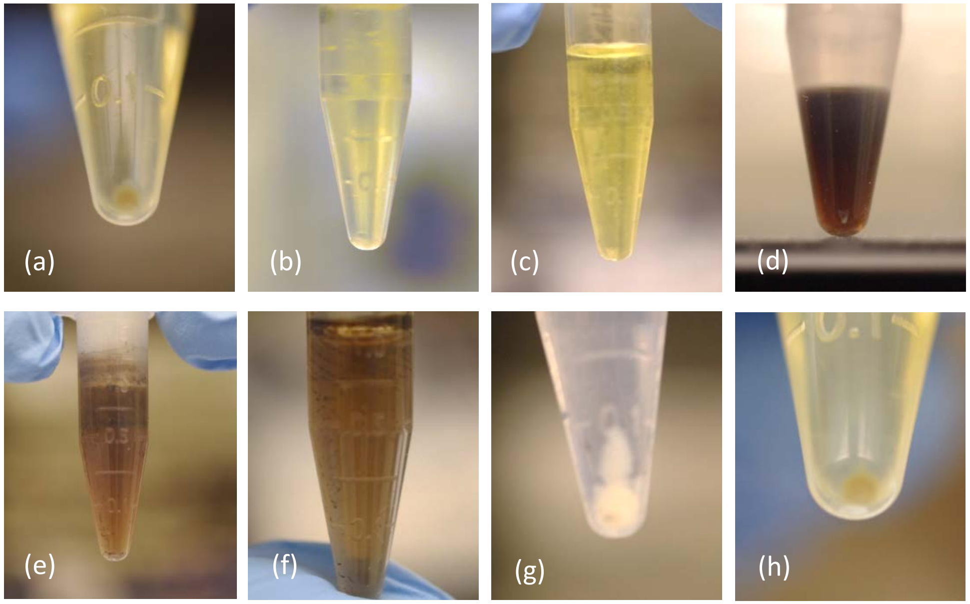


CNT Concentration, µg CNT/g CB (CNT mass, µg)	Recovery
10 (0.51)	160 ± 29%
54 (2.7)	99 ± 1.9%
220 (11)	96 ± 3.0%



Application – Rat lungs

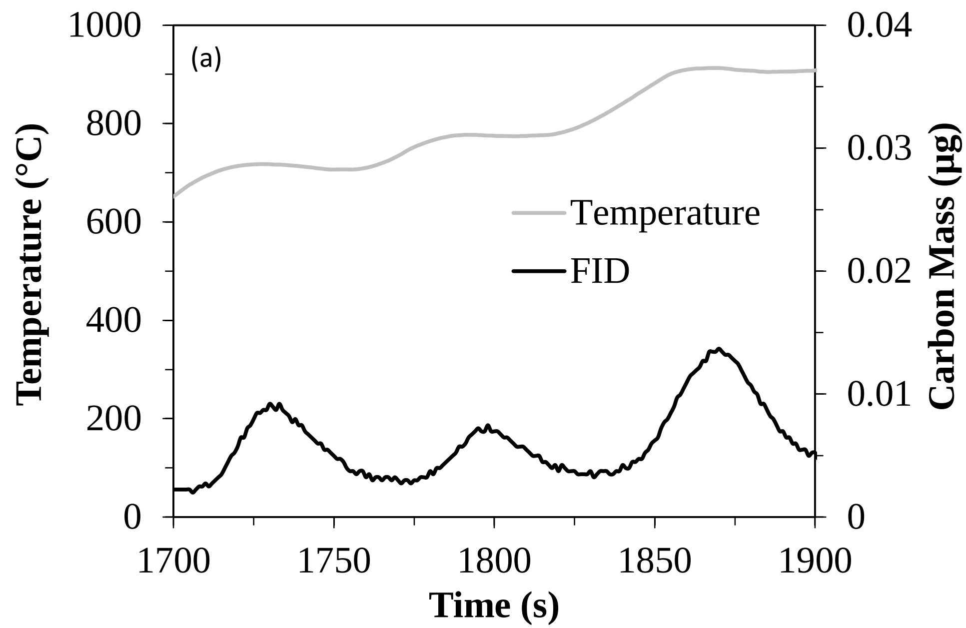
- Solvable, proteinase K, nitric acid, and ammonium hydroxide were optimal at dissolving tissue
- Solvable emerged as the best solution because of its ability to remove background carbon, form compact CNT pellets, and minimize damage to the instrument



Centirfuged rat lung tissue after treatment with the chemical digestion reagents: (a) Solvable, (b) hydroxide, (c) nitric, (d) sulfuric, (e) hydrochloric, (f) hydrofluoric, (g) peroxide, and (h) proteinase K.

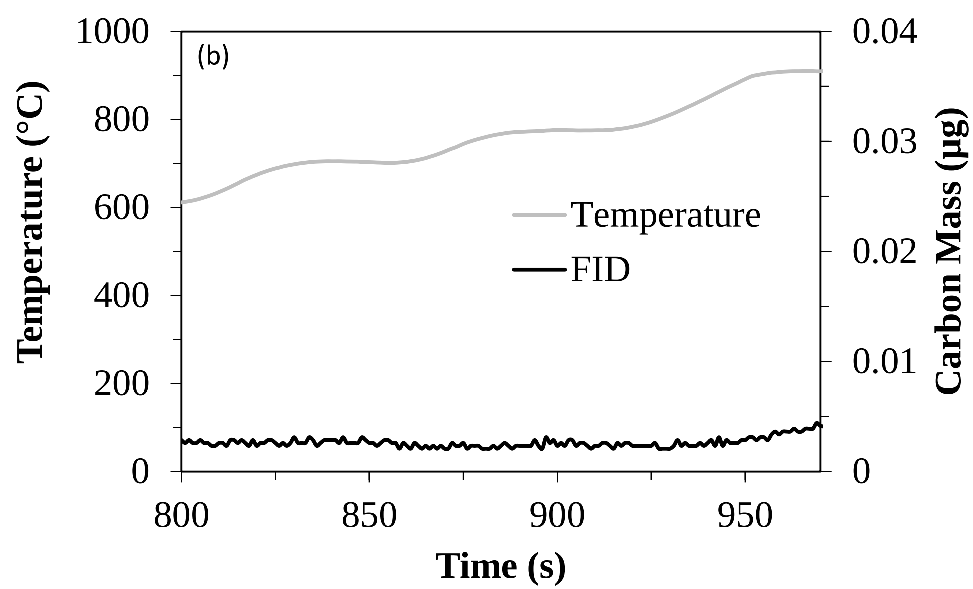
Rat lung tissue treatment with Solvable only

Some interference remains at higher temperatures where CNTs evolve

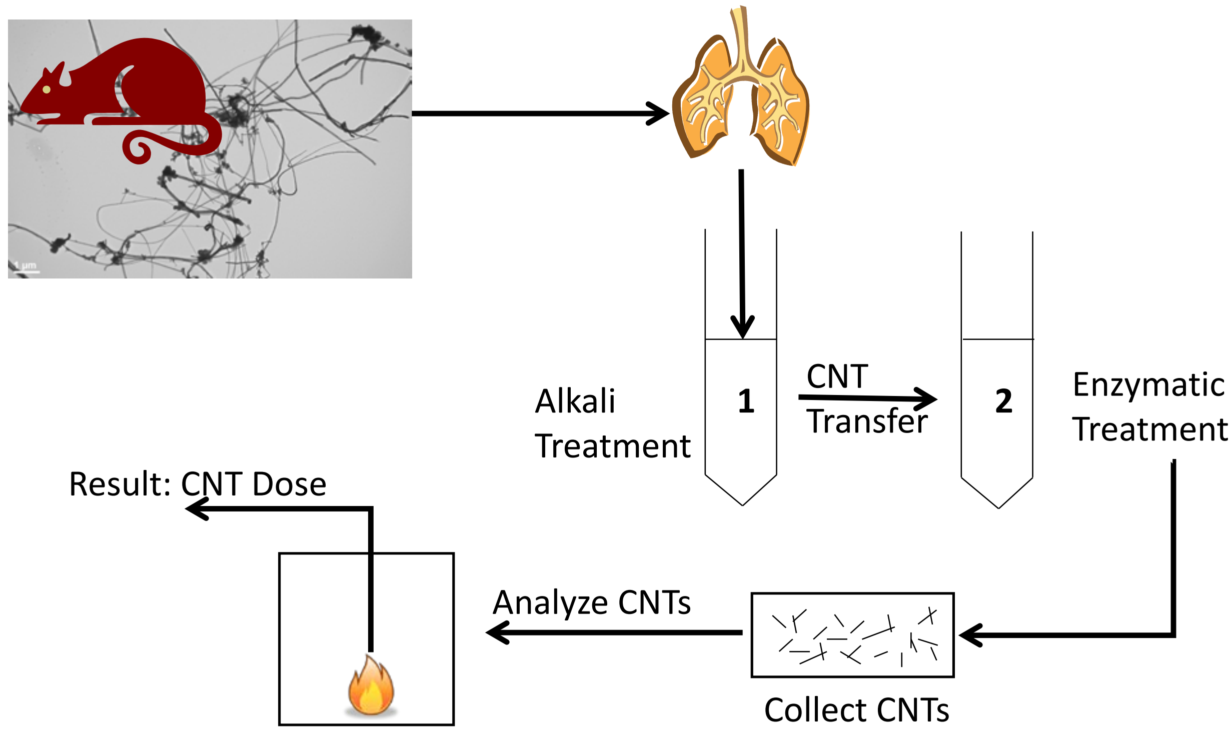


Rat lung tissue treatment with Solvable and proteinase K

Proteinase K successfully removed the remaining interfering carbon



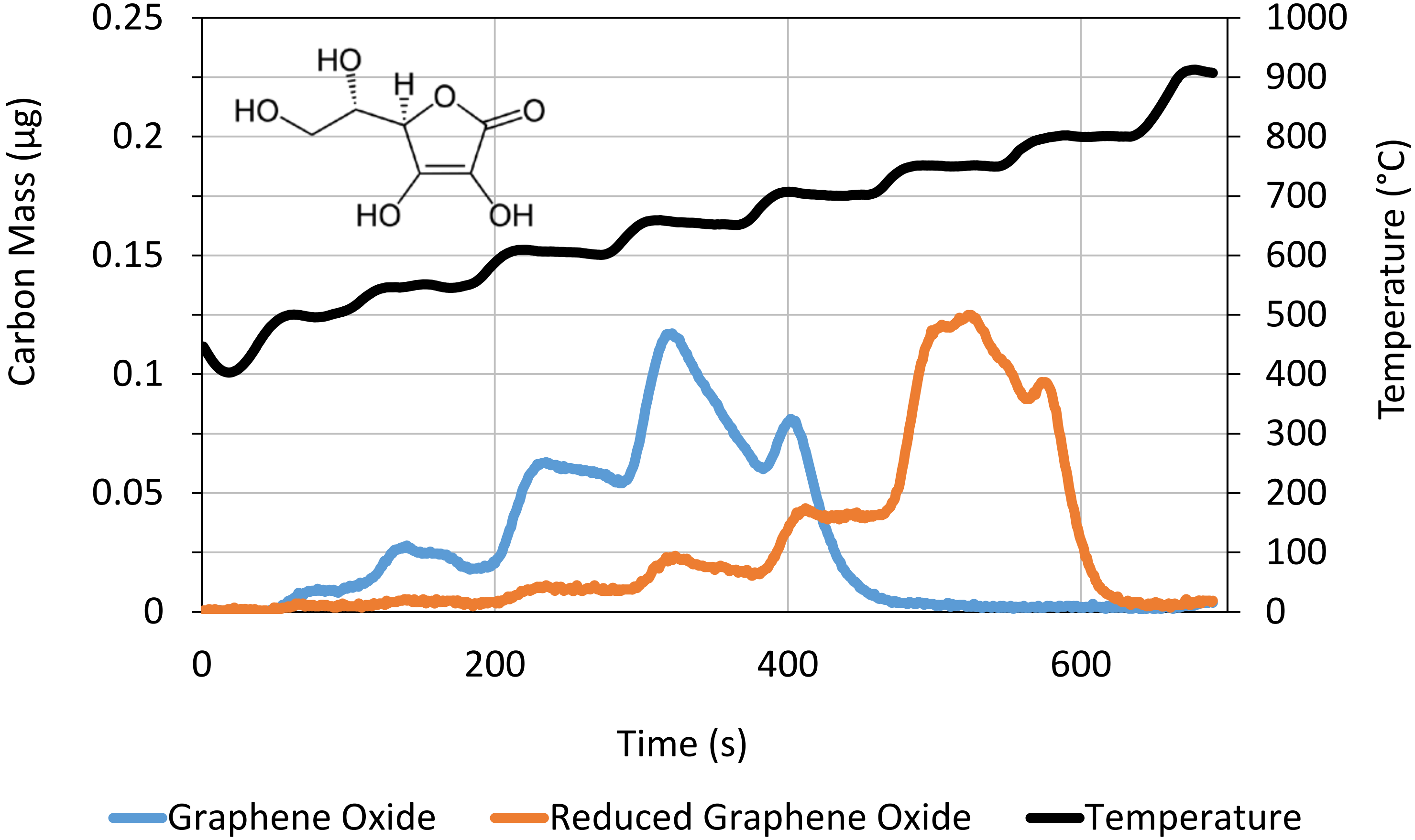
Extraction and quantification of CNTs in whole rat lungs



A recovery of 93±15% of a 3.6 μg body burden deposited in individual whole rat lungs was achieved.

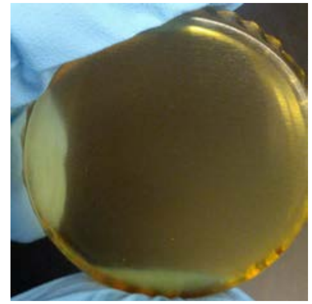
Graphene and *in-situ* reduction of graphene oxide

Graphene oxide has a 1:1 O:C ratio – How do we increase thermal strength?



Application – Composites

<u>Composite composition</u>
EPON 862 (Phenol-Formaldehyde Polymer Glycidyl Ether)
EPIKURE W (diethylmethylbenzenediamine)



Original

CNT

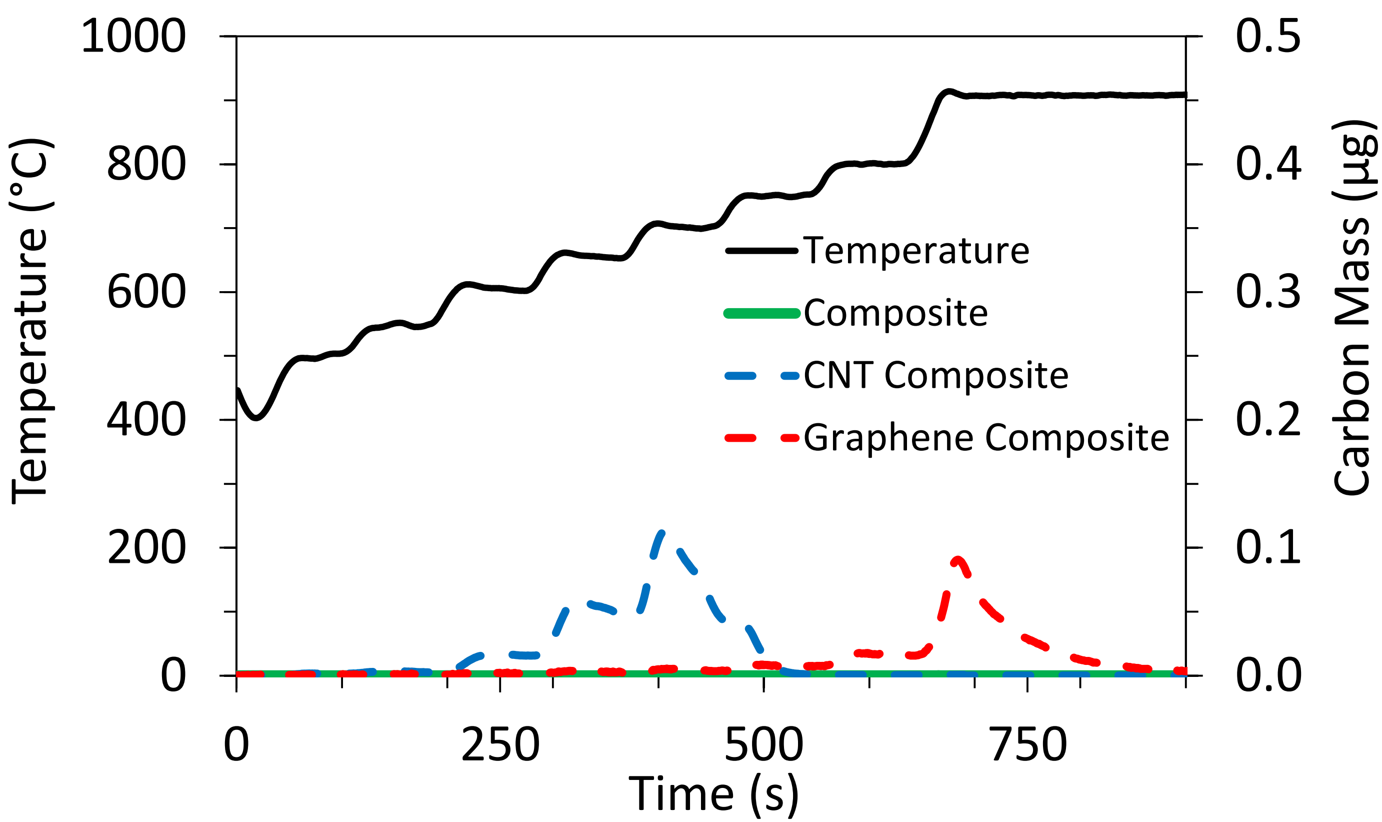
Graphene

CNT or Graphene shavings

Treatment →

CNT or Graphene pellet

Analysis of treated composite pellet



Going Forward

- Continue to develop extraction methods for other complex matrices (e.g., sediment)
- Develop alternative separation methods
- Finalize method for removing oxygen in-situ and examine effect on matrix carbon
- Is graphene and CNT separation possible?

Summary

- PTA is ideal for directly analyzing CNTs and graphene in simple matrices
- Extraction is necessary for complex matrices with embedded CNTs or a large amount of interfering carbon
- Extraction can also be used to concentrate samples with small CNT amount

Thanks!

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  - Rolf Halden
  - Pierre Herckes
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