Quantification of carbon nano materials in complex matrices

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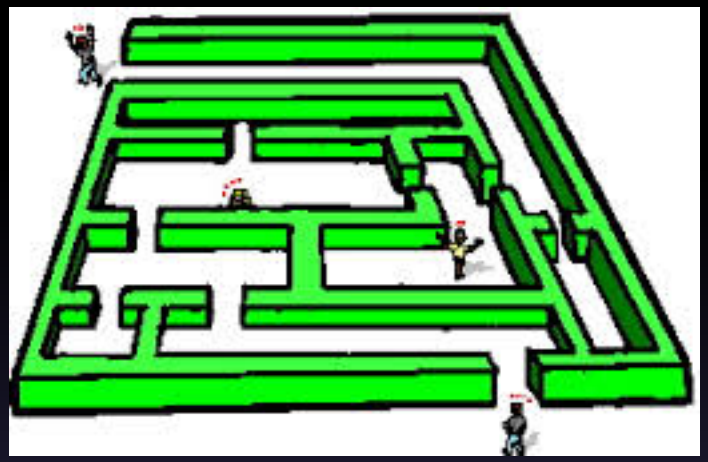
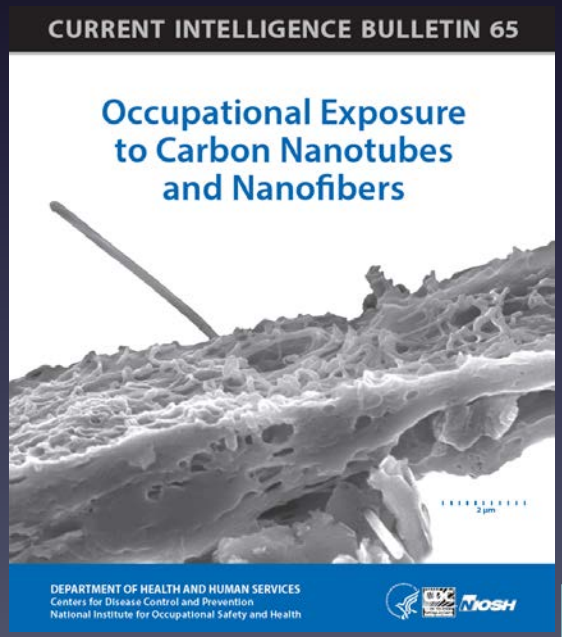
LC nano

Outline

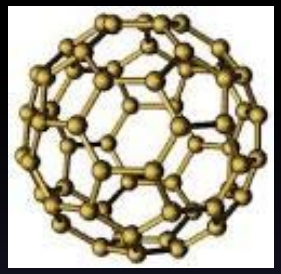
- 1D to 3D Types of Carbon
- Range of analytical techniques & response ranges
- Standards & Analytics
- Extraction / Separation Strategies
- Paths forward for Exposure monitoring





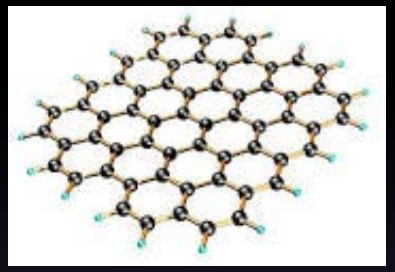
Types of Carbon Nanomaterials

$C_{60, 70, etc}$

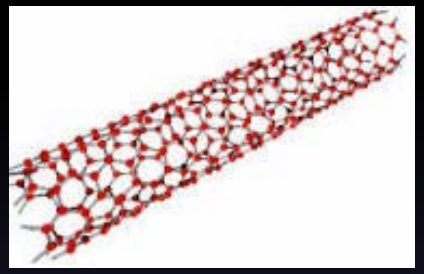


n C_{60}

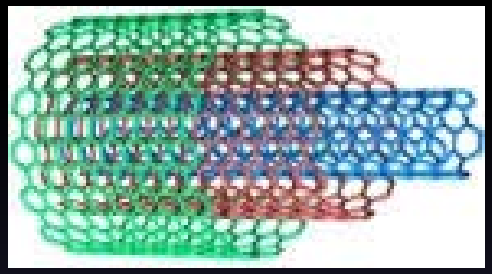
Few Layer Graphene



Single Wall CNT



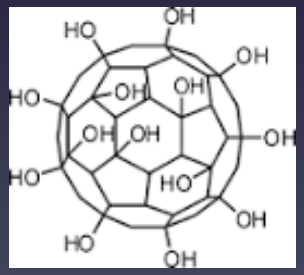
Multi- Wall CNT



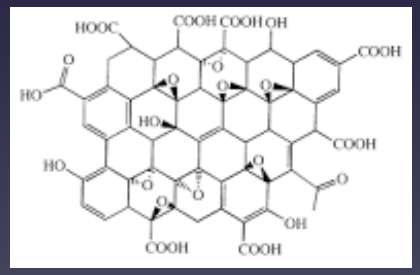
3 - D → 2 - D → 1 - D

720 Dalton → 10 Å (1nm) x μm^2 → 1-10 nm by µm-mm

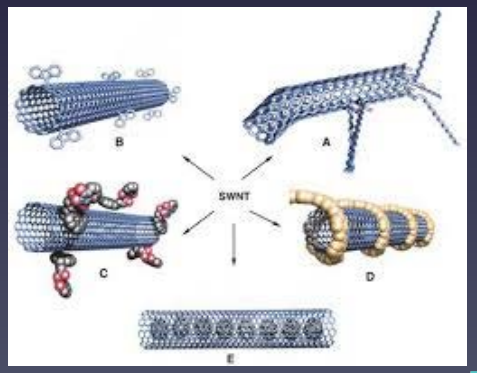
Wide Ranges of surface Functionalities can occur



Fullerol
(Hydroxy-fullerene)



Graphene-Oxide



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Quantification Techniques

Technique	C60 & nC60	FLG & GO	SW- & MW-CNT
Light scattering		✔	✔
Absorbance			
- UV	✔		
- NIR fluorescence			✔
- Gel electrophesis			✔
HPLC-UV (FFF-UV)	✔		
LC-Mass Spec	✔		
Thermal			
- Combustion / CO/CH4	✔	✔	✔
- Microwave induced heat			✔
- TGA mass loss		✔	✔
^{14}C			
Scintillation	✔	✔	✔
Thermal-Mass spec	✔		✔
Raman spec.		✔	✔
Photo-acoustic/thermal			✔
Single particle ICP-MS of catalyst			✔

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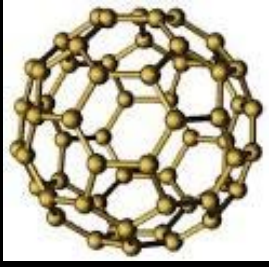
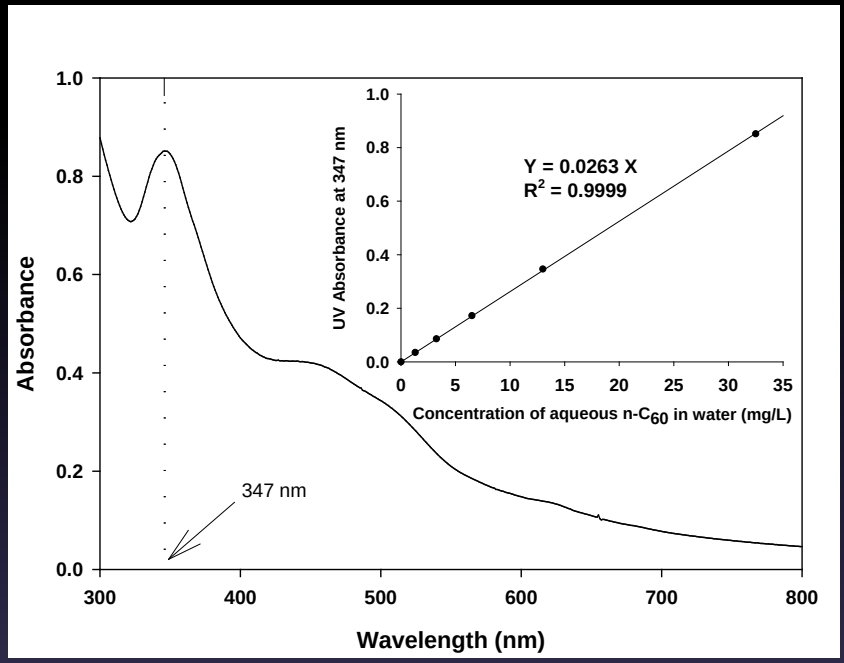
Examples – Fullerenes (C_{60})



- Light scattering ($\lambda_{347\ nm}$)
- Liquid phase combustion (TOC)
- Thermal optical transmittance
- HPLC plus $\lambda_{347\ nm}$
- LC/MS using 720 m/z



Improving specificity and lower detection limits

Chen et al., 2008

C_{60} analysis by HPLC-UV or –MS Requires Solvent Extraction

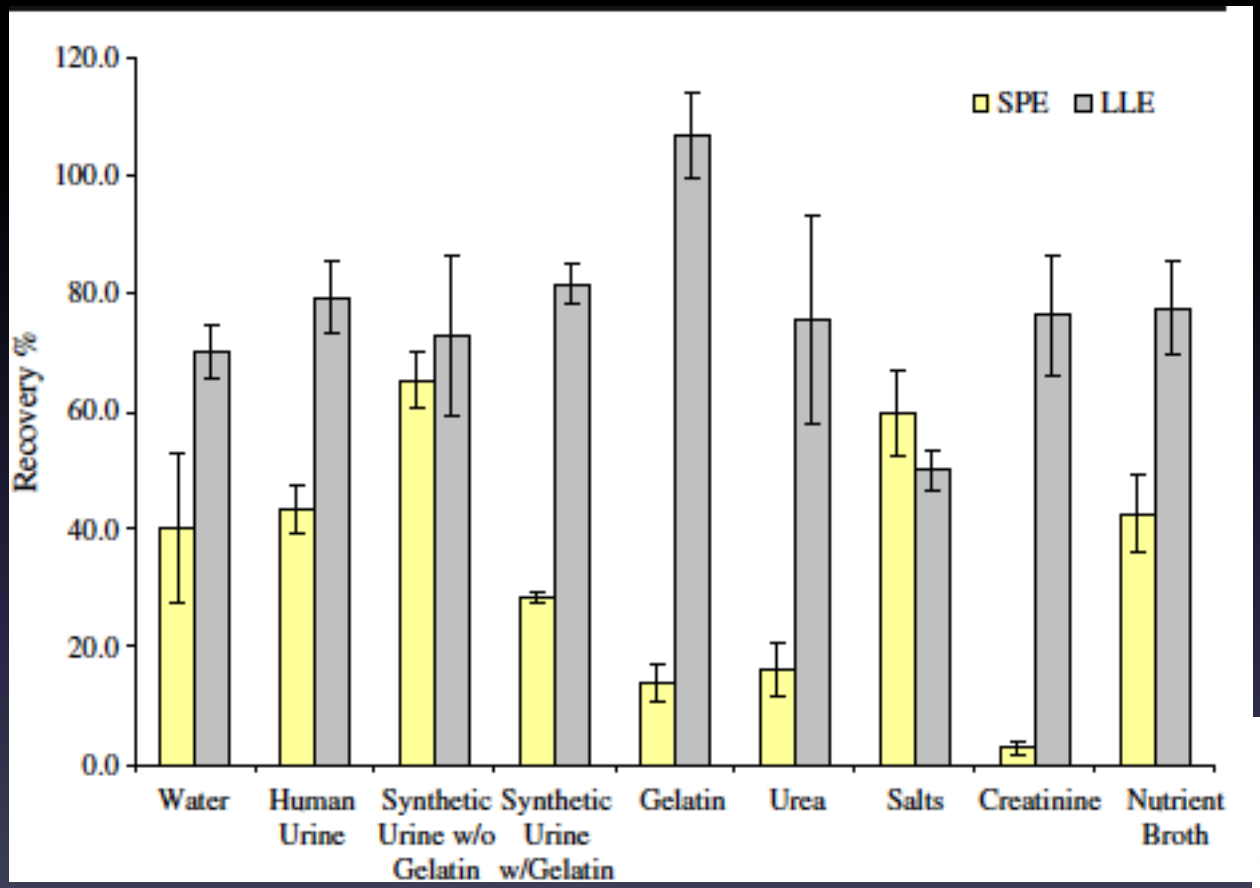
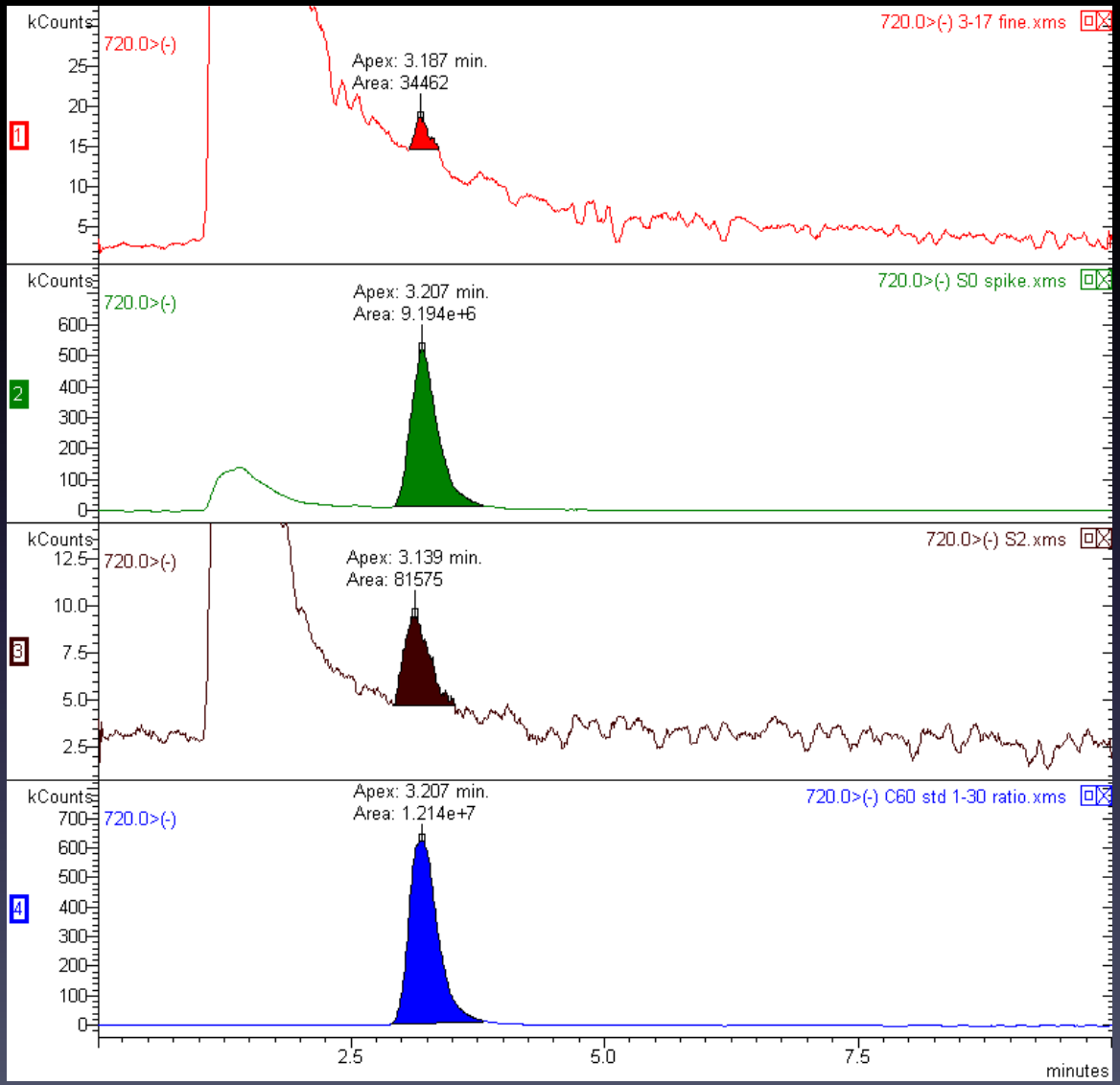


Fig. 3 Recovery of C_{60} from synthetic and human urine matrices using LLE and SPE. C_{60} was spiked to a final concentration of 180 µg/L and allowed to equilibrate in the media overnight. *Error bars* indicate the variability in quantification between three extractions of each sample matrix

Benn et al., ABC, 2011

Application of LC/MS



C_{60} detection in

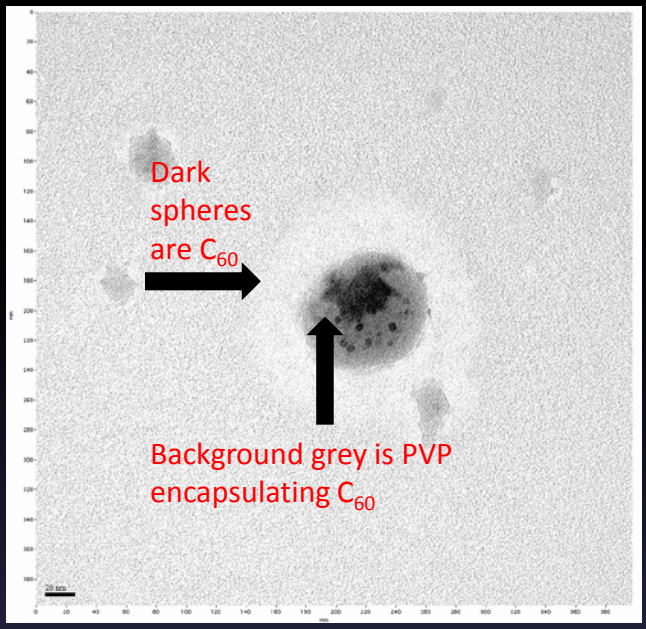
a) a parking garage air sample of PM2.5,

b)a filtered air sample spiked with C_{60},

c) a parking garage air sample of size > PM2.5,

d) C_{60} standard; Detection limit ~500 ng/L

Fullerenes From Cosmetics



- **A common cosmetic formulation disperses fullerenes using polyvinylpyrrolidone (C_{60}-PVP)- see TEM**
- LC/SM was used to separate and specifically detect fullerenes (C_{60} and C_{70}) from interfering substances typically present in cosmetics (e.g., castor oil).
- **C_{60} was detected in 4/5 commercial cosmetics ranging from 0.04 to 1.1 µg/g, and C_{70} was qualitatively detected in 2/5 samples**.
- A single-use quantity of cosmetic (0.5 g) may contain up to 0.6 µg of C_{60} and demonstrates a pathway for human exposure to engineered fullerenes.

Benn et al., Environ. Poll. (2011)

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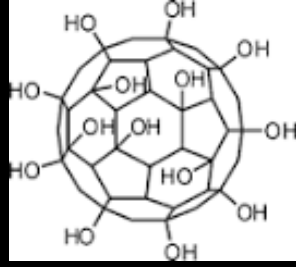
Fullerols ($C_{60}(O)$, etc)



- Light scattering ($\lambda_{347\ nm}$)
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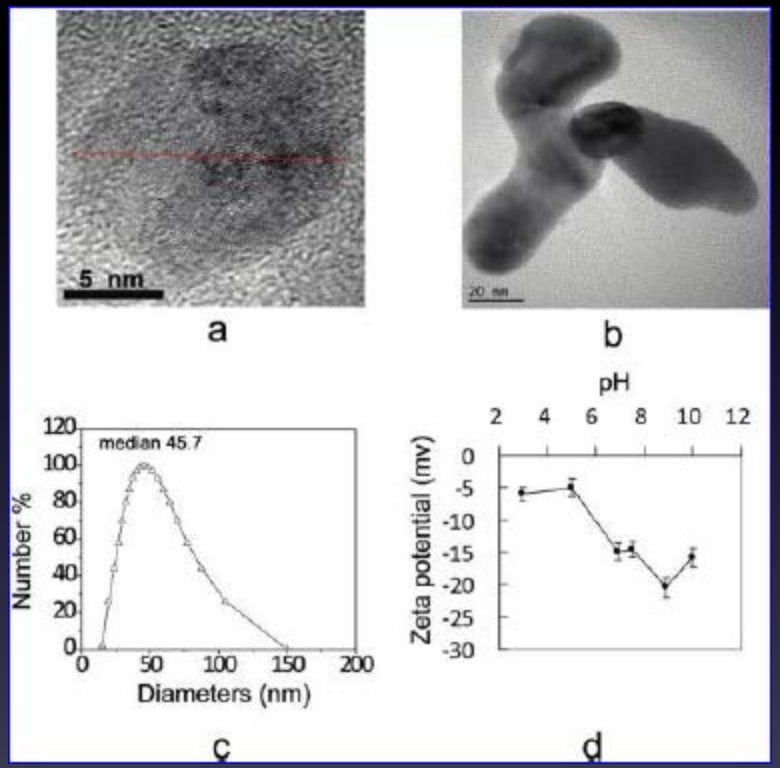
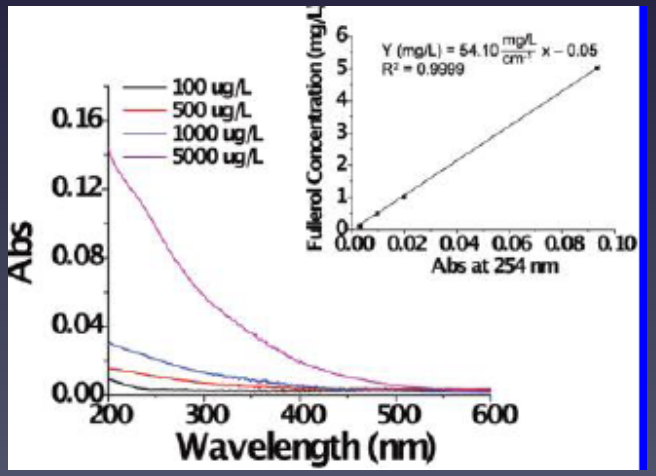
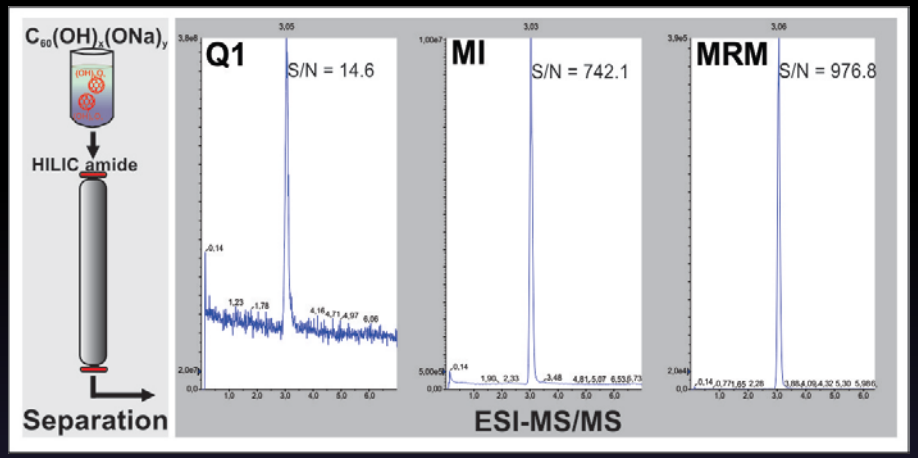
- LC/MS using 720 m/z





Chao et al., 2011

Fullerol – Comparison of Detection Methods

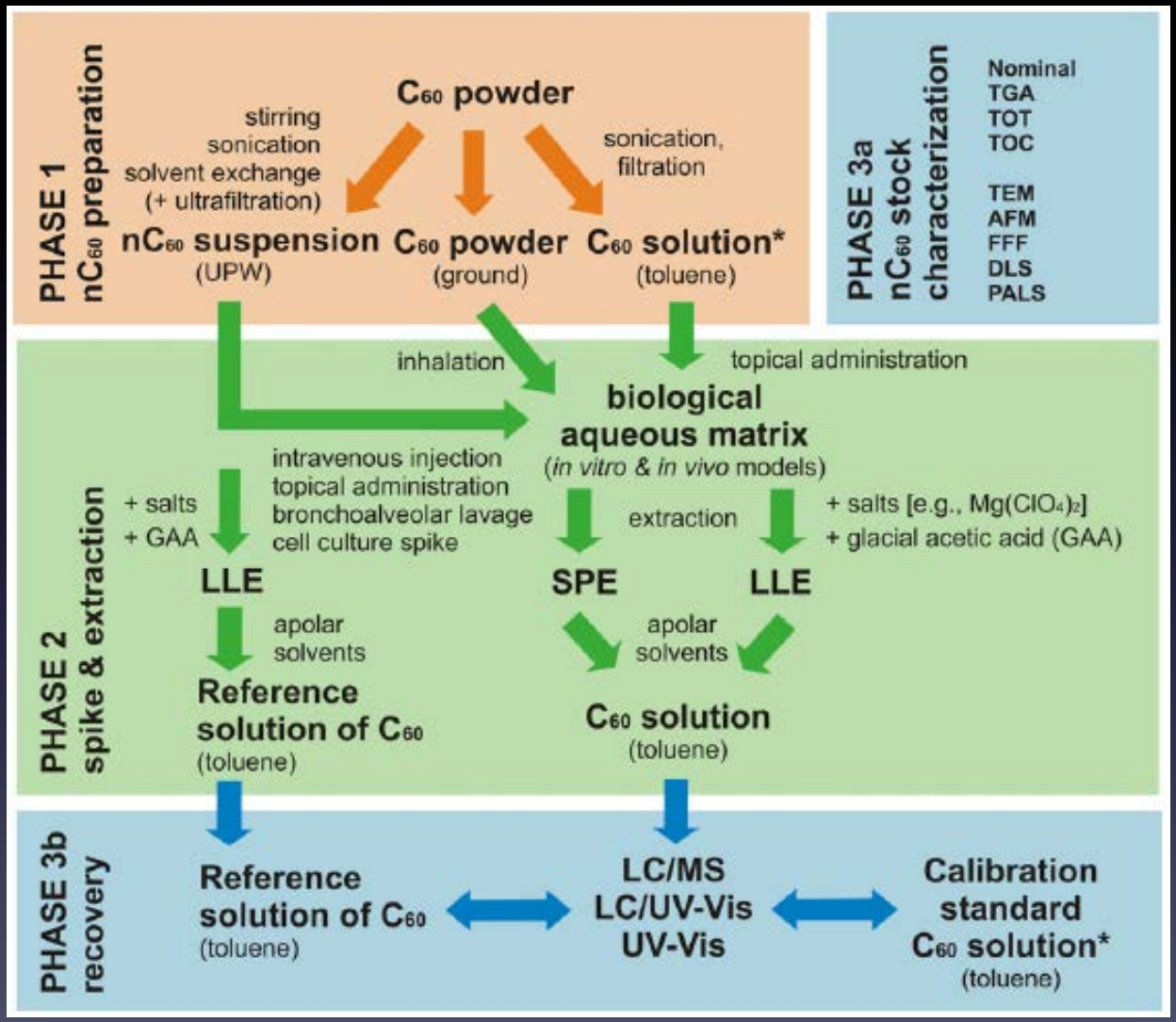


single quad scan, Q1
multiple ion monitoring, MI
MS with multiple reaction monitoring, MRM

No standards available

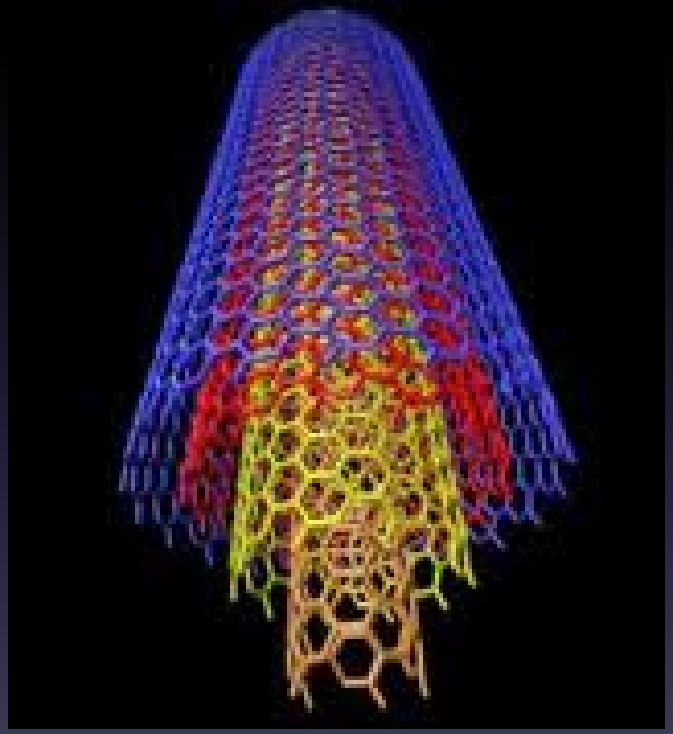
	R^2 [a]	MDL [b] [pg/mL]	RSD [c]	SRFA [d]
UV/Vis	0.999	42 780	n.d.	n.d.
Q1 scan	0.9996	125	2.9 %	29.4 %
MI scan	0.9999	1.5	0.7%	8.6 %
MRM scan	0.9999	0.19	0.5 %	2.5 %

Fullerene Summary

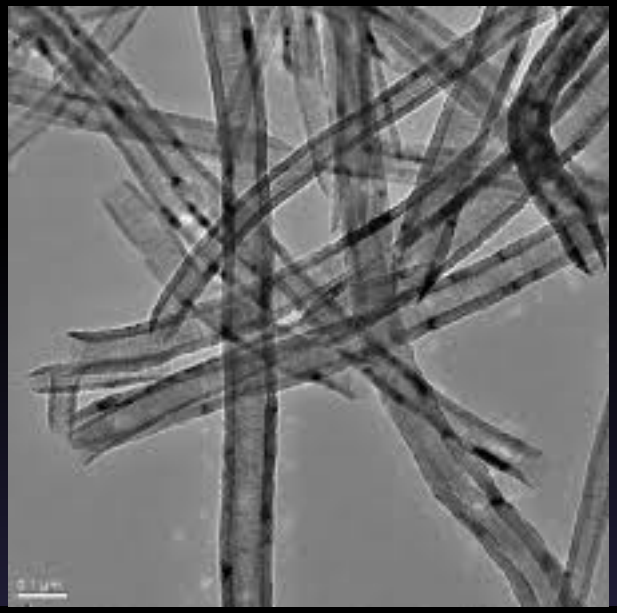


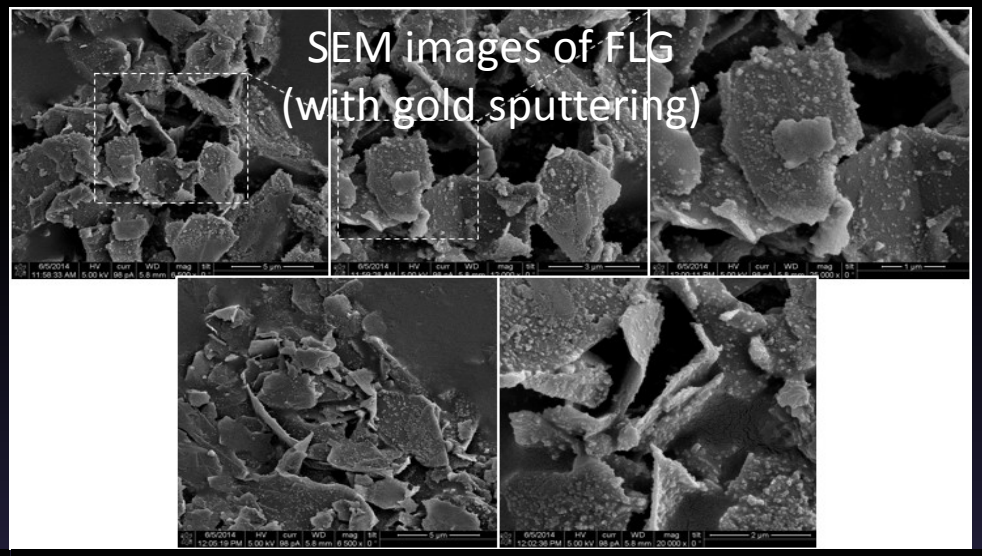
Pycke et al., 2011

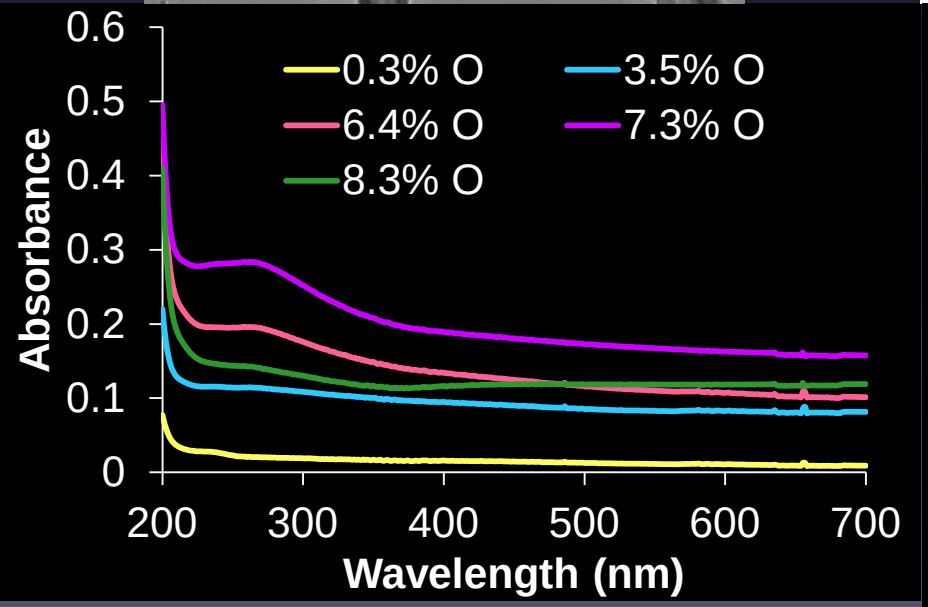
Quantification – CNTs

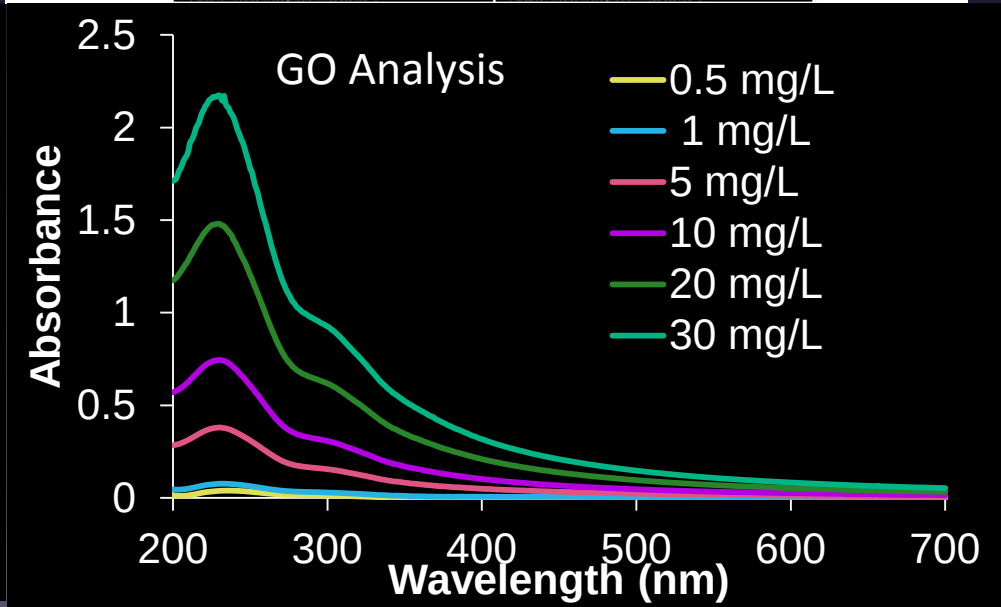


CNT & Graphene UV/VIS Absorbance

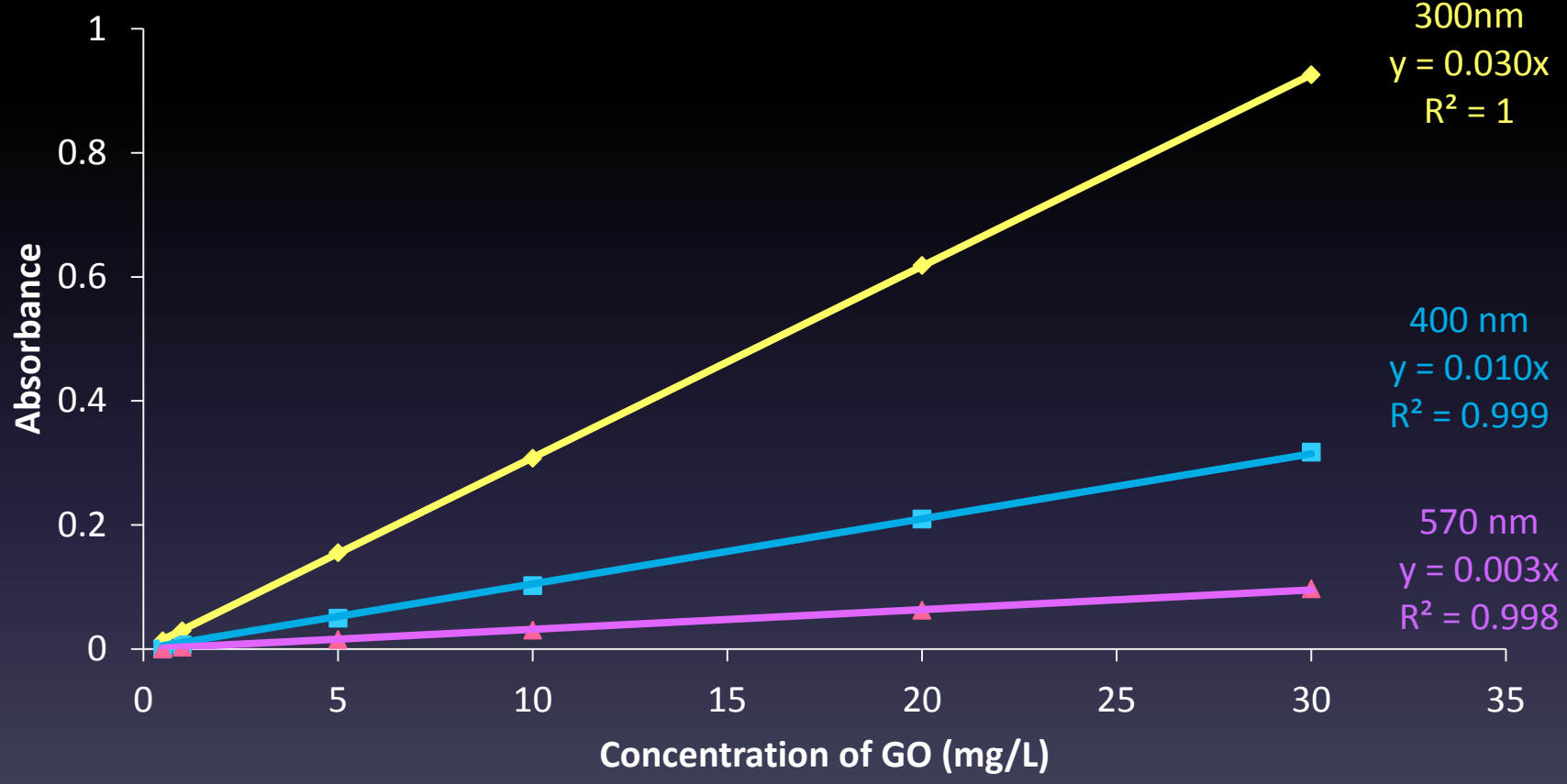








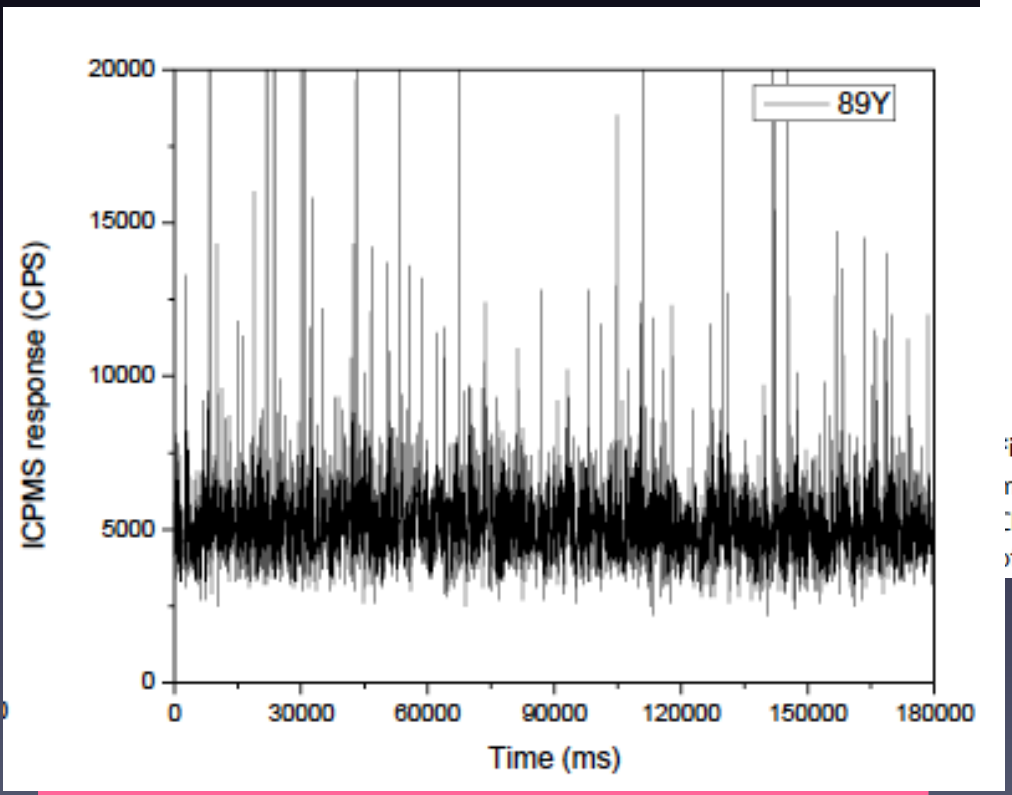
Standard curve for GO at different wavelengths

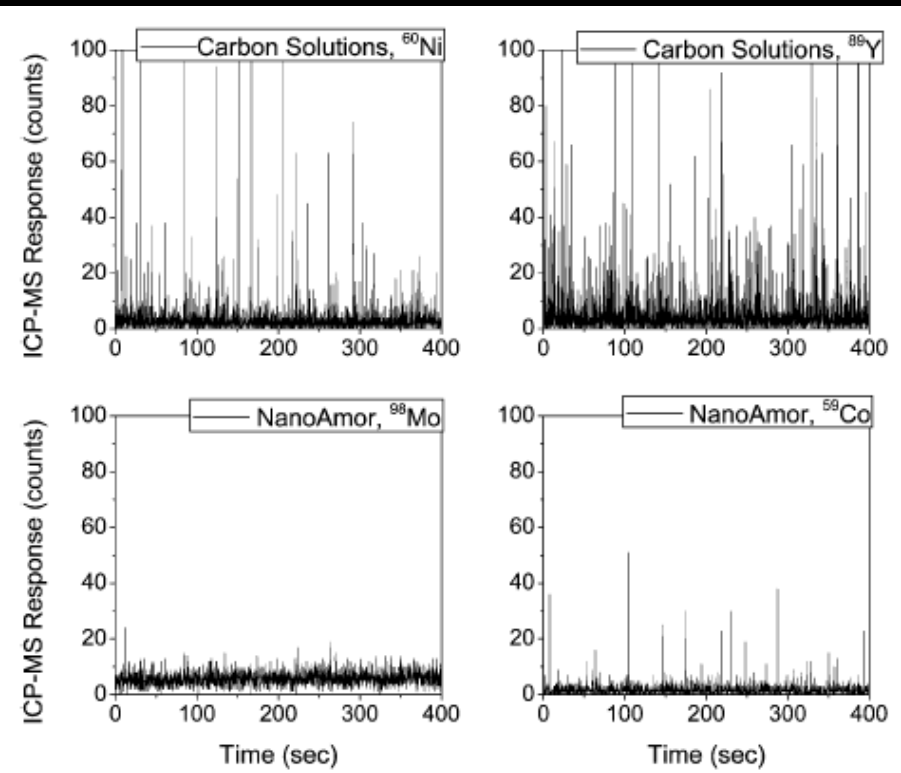


Indirect Measurement

Reed et al., 2013

- Single Particle ICP-MS (spICP-MS)
  - Track residual catalyst rather than carbon
  - Ranville et al. showed for SWCNT
  - Our group has evidence for MWCNT



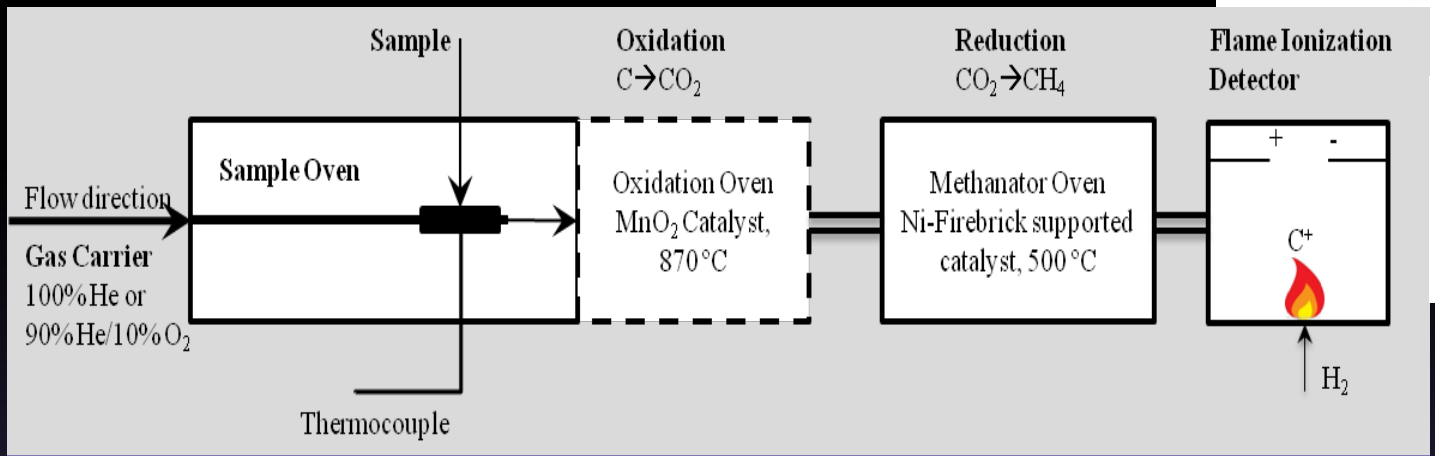


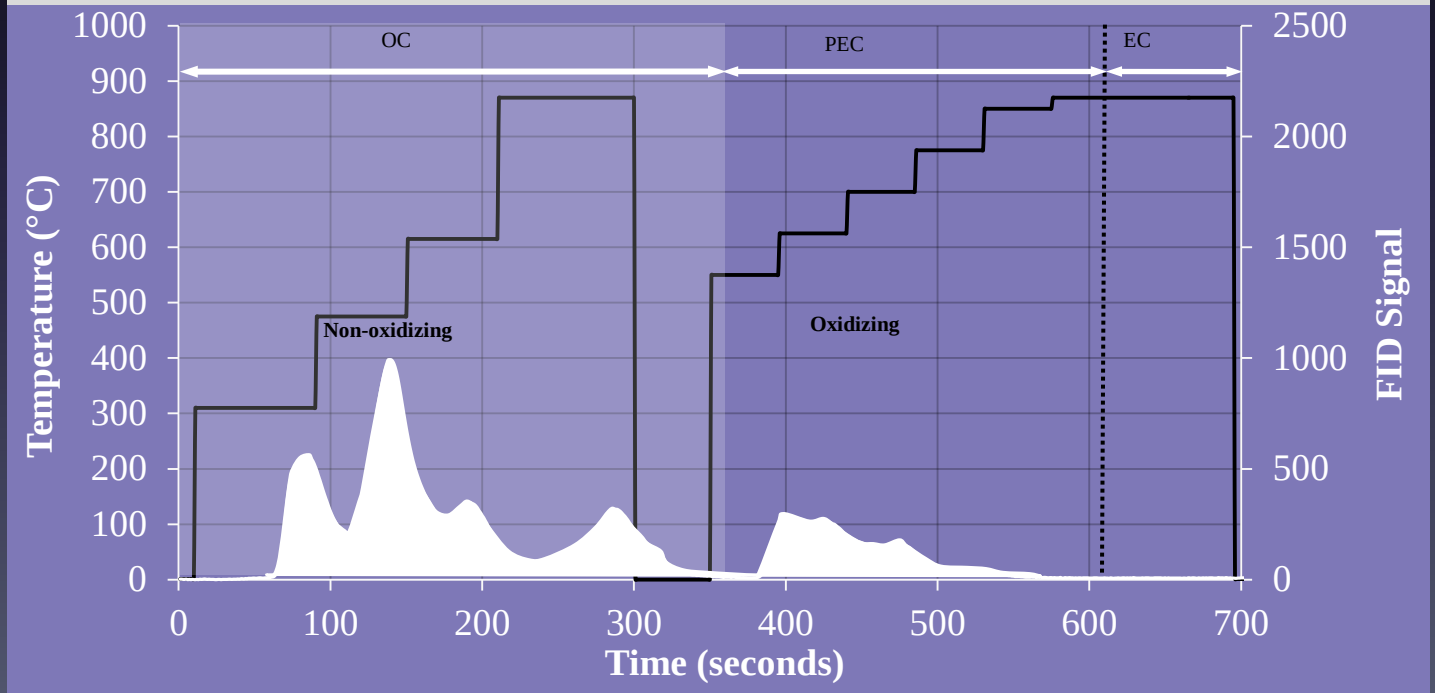
ig. 1 Real-time ICP-MS response data, for determination of the best analyte netal for CNTs used in this study. The CNTs were at 1 ug L^{-1} to ensure enough CNTs would be in solution for analyte comparison. Only data for one isotope each of Ni (^{60}Ni) and Mo (^{98}Mo) are shown here. Other isotopes were not as usable due

Pulses ≈? ≈ CNTs

Thermal Optical Transmittance (Temperature Programmed Oxidation)

Sunset Laboratories Lab OC-EC Aerosol Analyzer





Comparison of 15 CNTs

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

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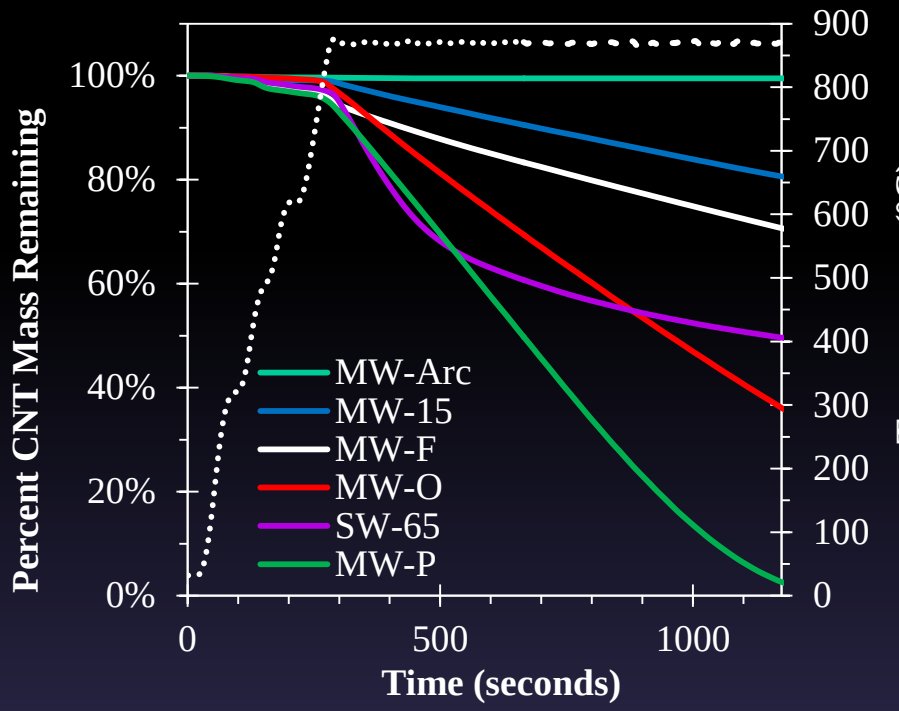
Thermal Properties of CNTs

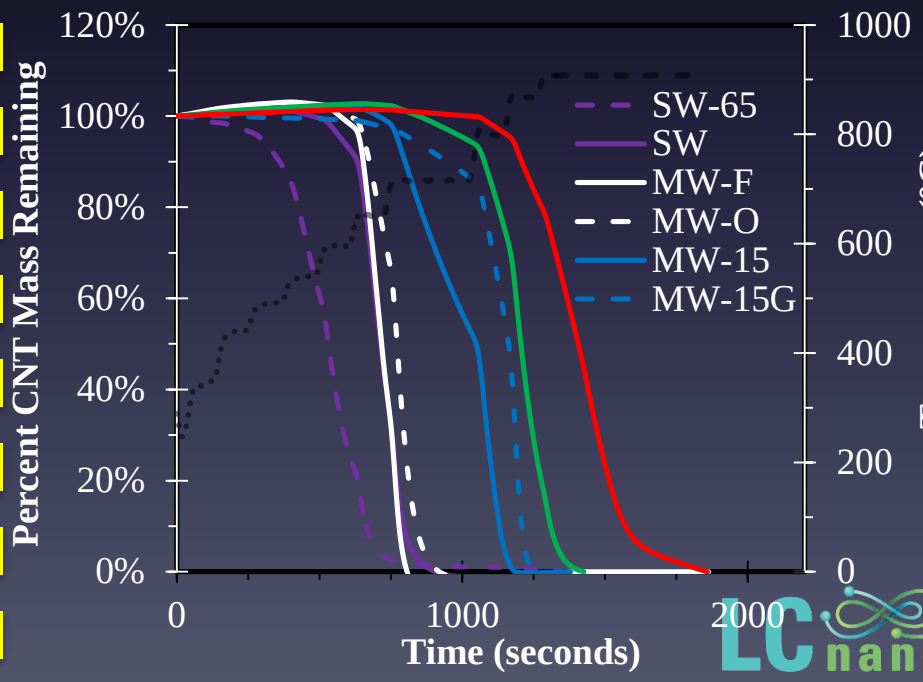


Inert conditions (100% He)

Conclusion: Surface oxygen groups allow some CNTs to burn in inert gas environment

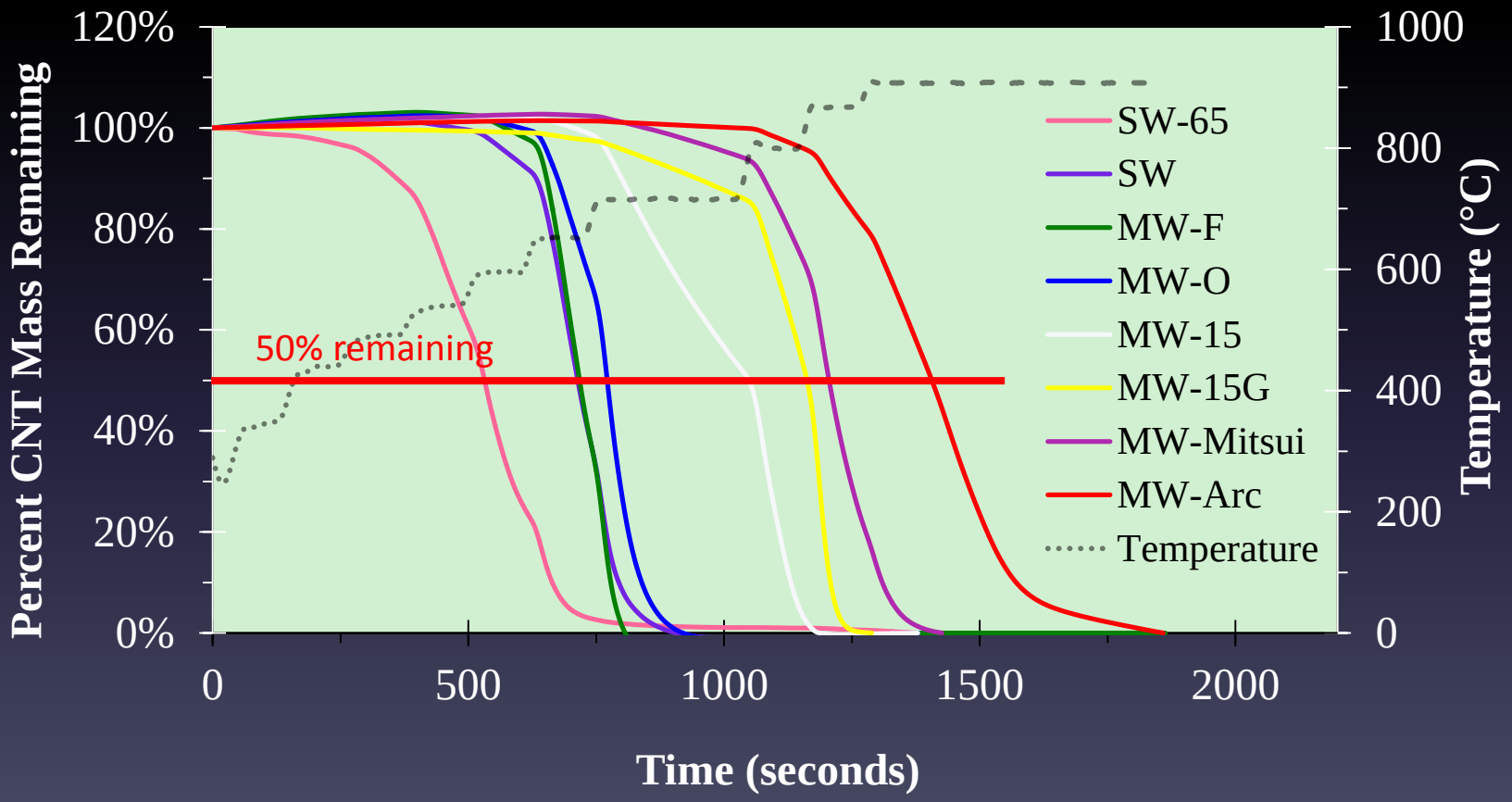
Oxidizing conditions
(90% He/ 10% O_2)

Conclusion: Not all CNTs "burn" at the same temperature



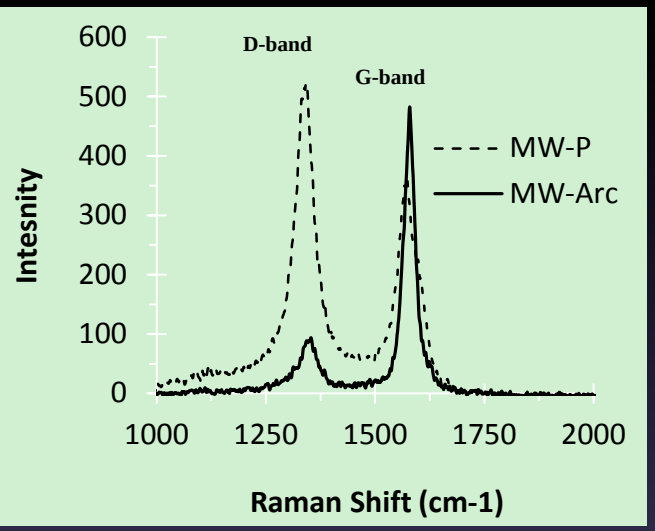
Temperature Comparison for 50% CNT combustion

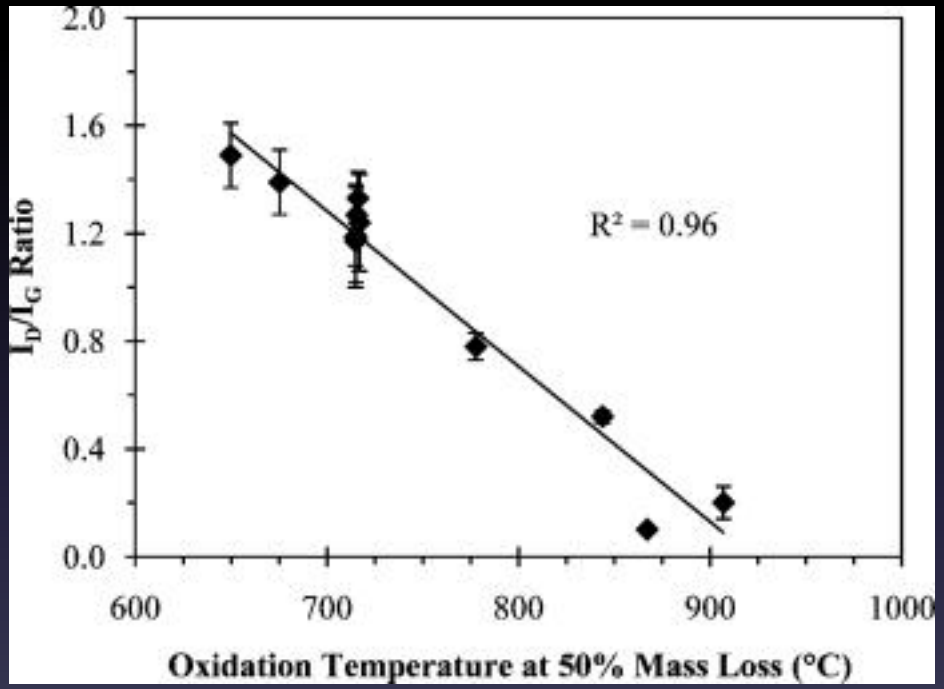
PTA method is a refinement to NIOSH Method 5040

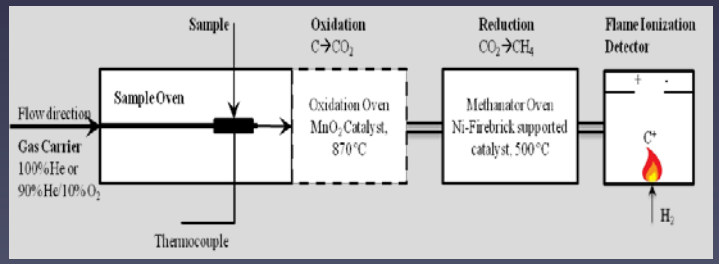


Doudrick, K., P. Herckes, P. Westerhoff. Detection of carbon nanotubes in environmental matrices using programmed thermal analysis. *Environ. Sci. Technol.*, 46(22), 12246–12253, 2012.

Thermal Properties of CNTs related to Structural Defects

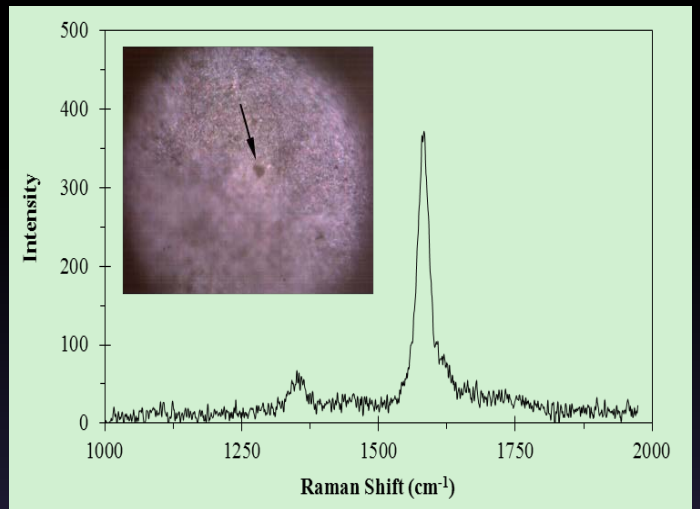




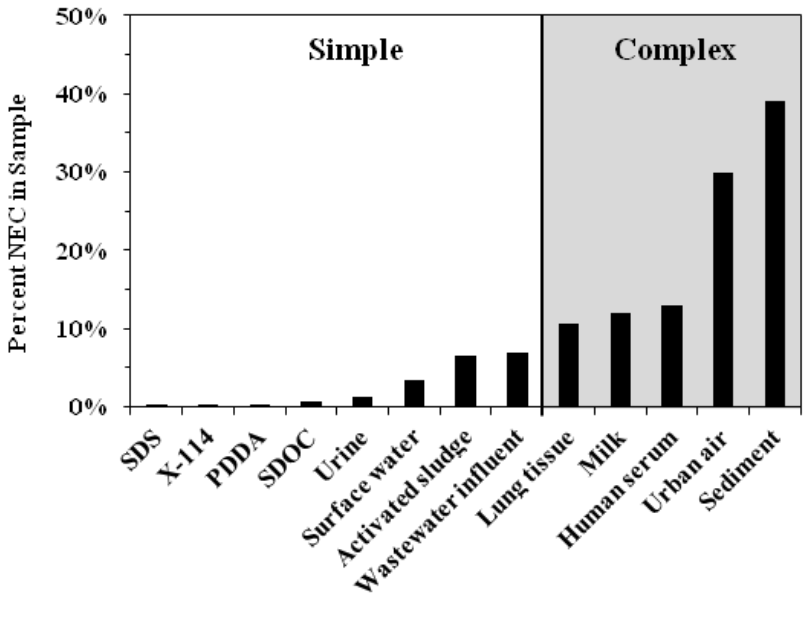


CNTs & Other NM Detection in biomass

- Raman and imaging can detect CNTs, but not quantify them well

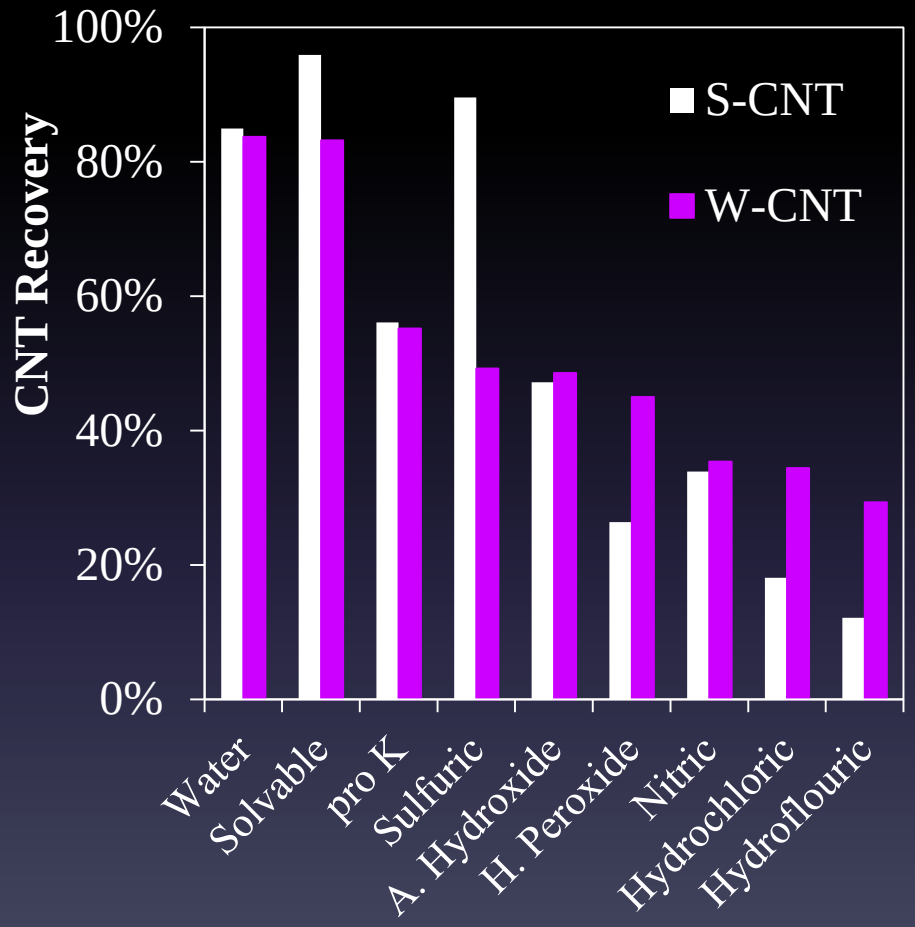


- Extraction protocol must:
  - Minimize oxidation of CNT
  - Remove interfering background organic carbon (from rat lung tissue)
  - Separate solid-phase CNT from liquid-phase dissolved tissue



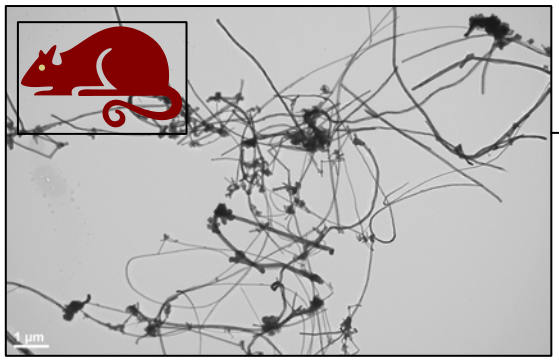
Selective digestion can remove organic matter & facilitate CNT quantification

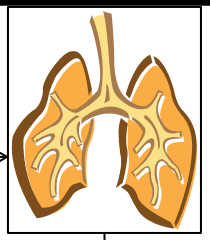
- Can solvents remove organic matter?
  - Yes
  - Oxidants (H_2O_2)
  - Acids (HNO_3, H_2SO_4)
  - Alkali (NaOH, KOH, NH_4OH, Solvable)
  - Enzymes (TMAH, ProtK)
- But, do solvents affect CNT detection?
  - Mostly, yes
  - Surface oxygenation results in combustion at lower temperatures
  - Enymes and customized alkali fair best



Doudrick, K., Corson, N., Oberdörster, G., Eder, A., Herckes, P., Westerhoff, P. Extraction of carbon nanotubes from rat lung tissue. *ACS Nano (2013)*

Application of Extraction Method to Rat Lungs





Alkali Treatment (Solvable)

1

CNT Transfer

2

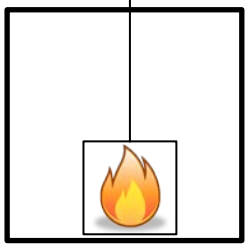
Enzymatic Treatment (Proteinase K)

Wash/Centrifuge

Collect CNTs

Analyze CNTs

Result: CNT Dose

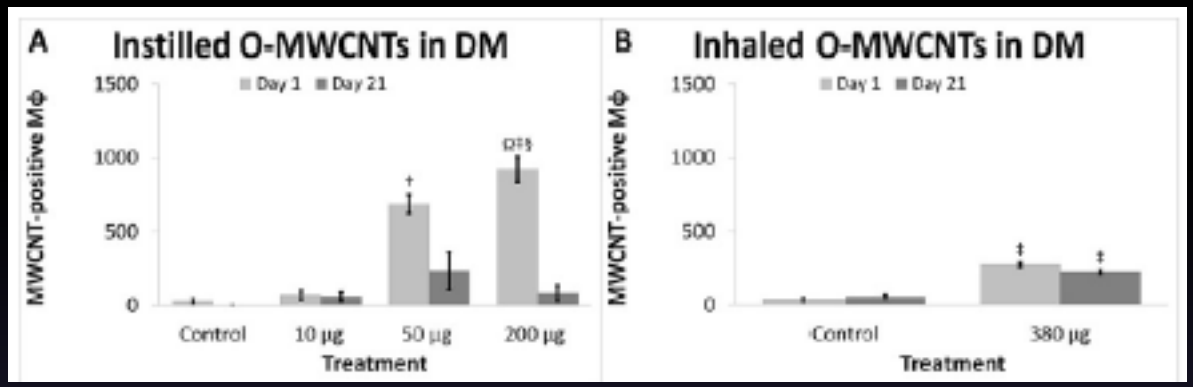


2.9 ±0.19 µg CNTs, whole lung – 93% recovery

Doudrick, K., Corson, N., Oberdörster, G., Eder, A., Herckes, P., Westerhoff, P. Extraction of carbon nanotubes from rat lung tissue. *ACS Nano* (*2013*).

Microsoft clipart

Hazard & Exposure Analyses



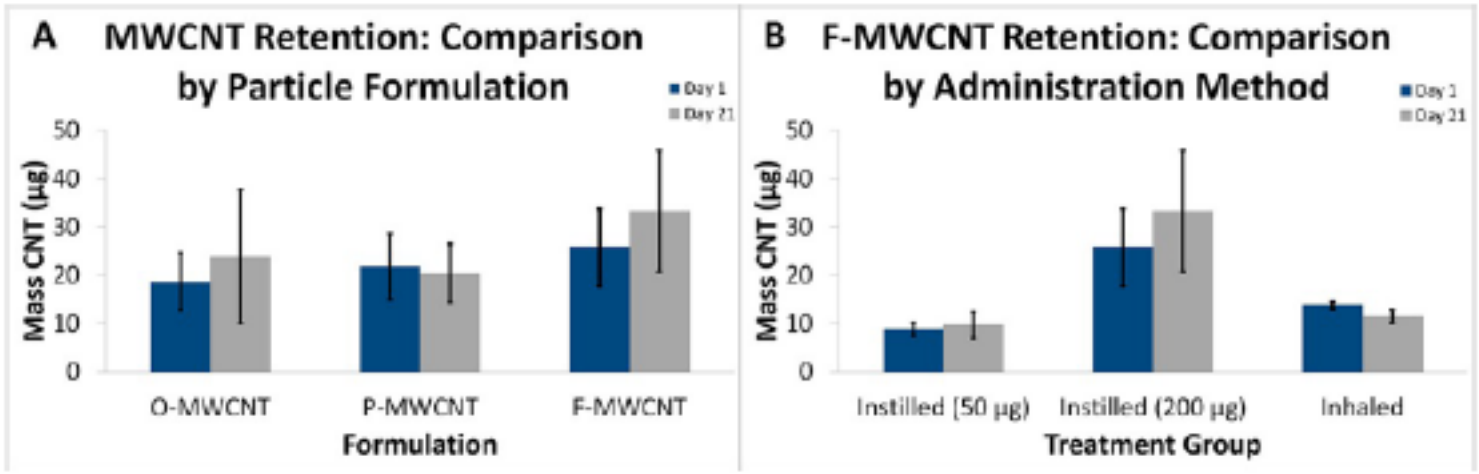
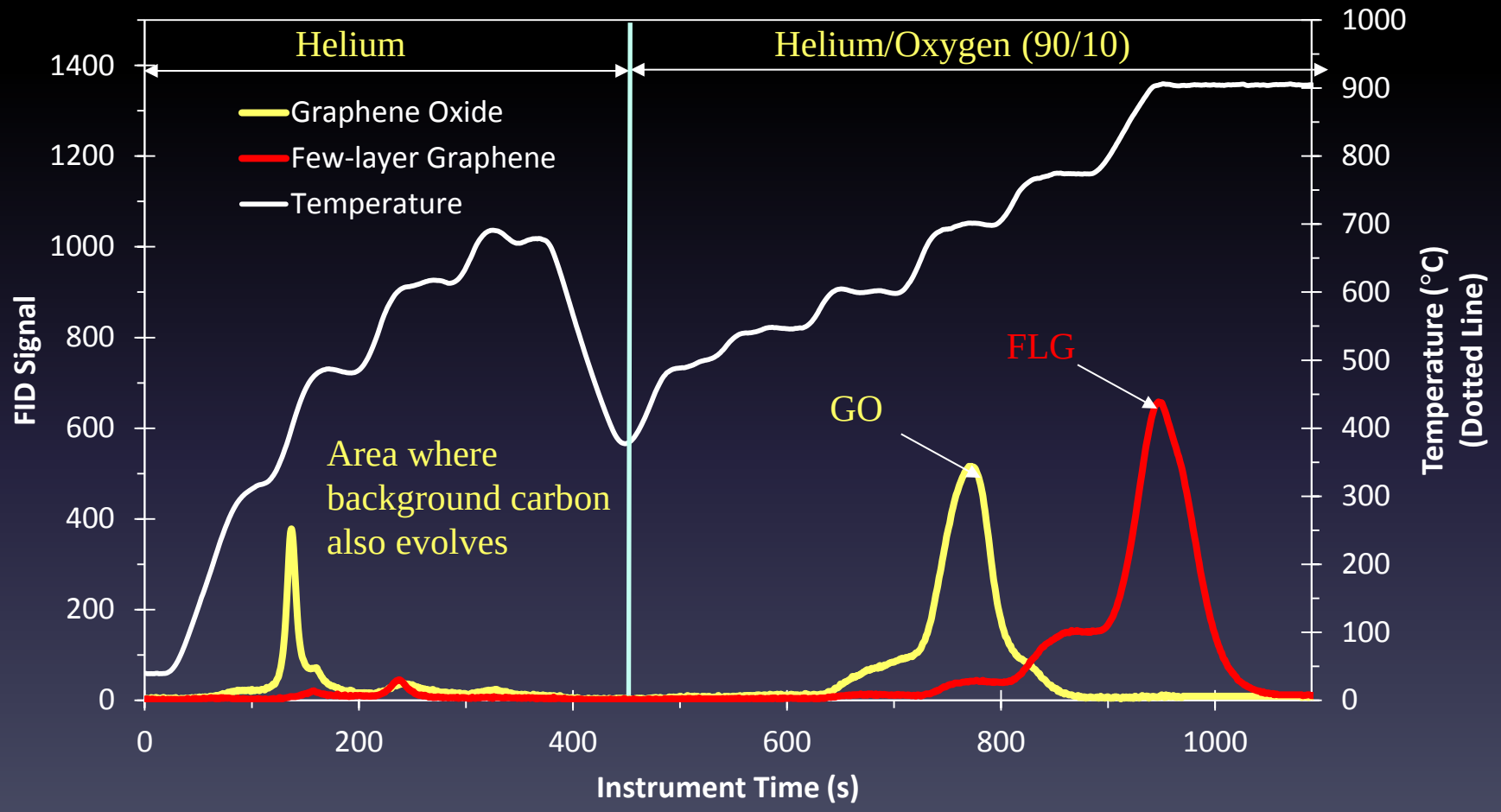


Figure 12. Programmed thermal analysis quantification of MWCNTs in lung tissue. (A) Day 1 and 21 time-course data from animals instilled with O-, P-, or F-MWCNTs. (B) Time-course data from animals exposed to F-MWCNTs by intratracheal instillation and inhalation.

Silva et al., ACS Nano, 2013

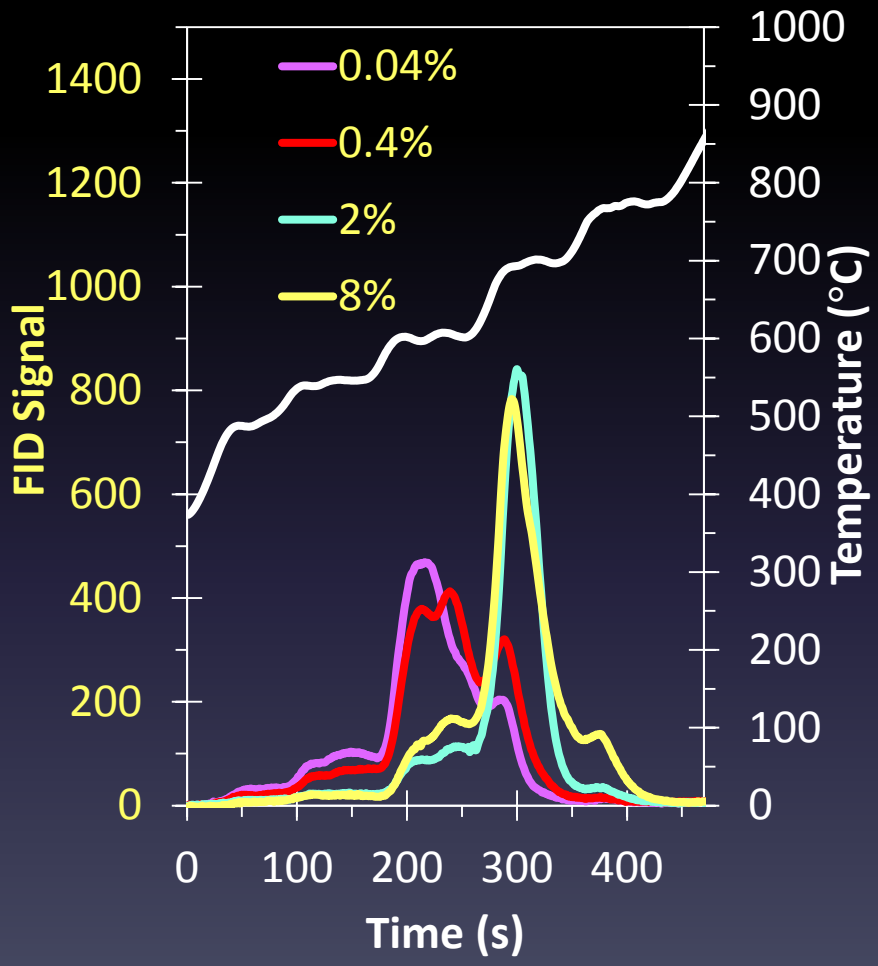
Similar Approach for Graphene (GO & FLG)

Step 1- Programmed Thermal Analysis (PTA)



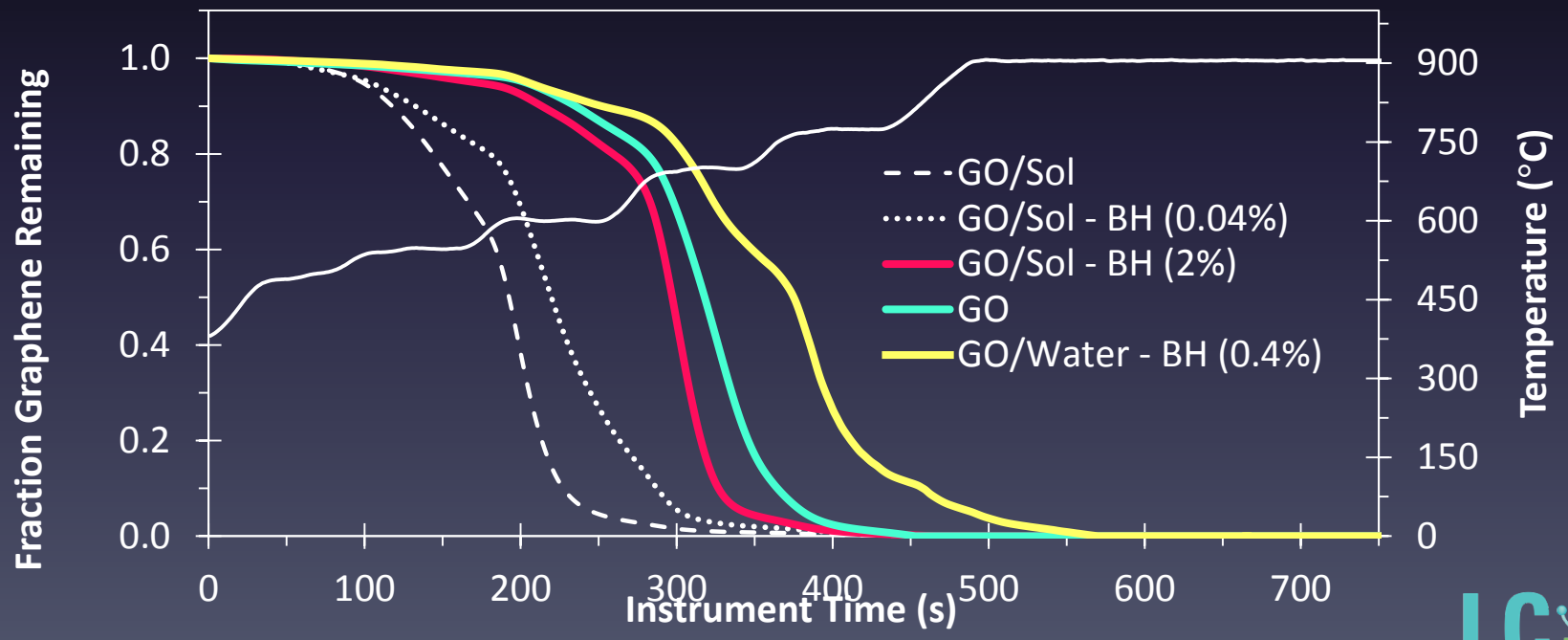
Step 2: Improve separation of GO signal from background organics

- Add reductant ($NaBH_4$)
- Reduced graphene oxide (RGO) analysis by XPS yields decreases number of C-O & C=O bonds by > 5 fold
- PTA thermogram improves

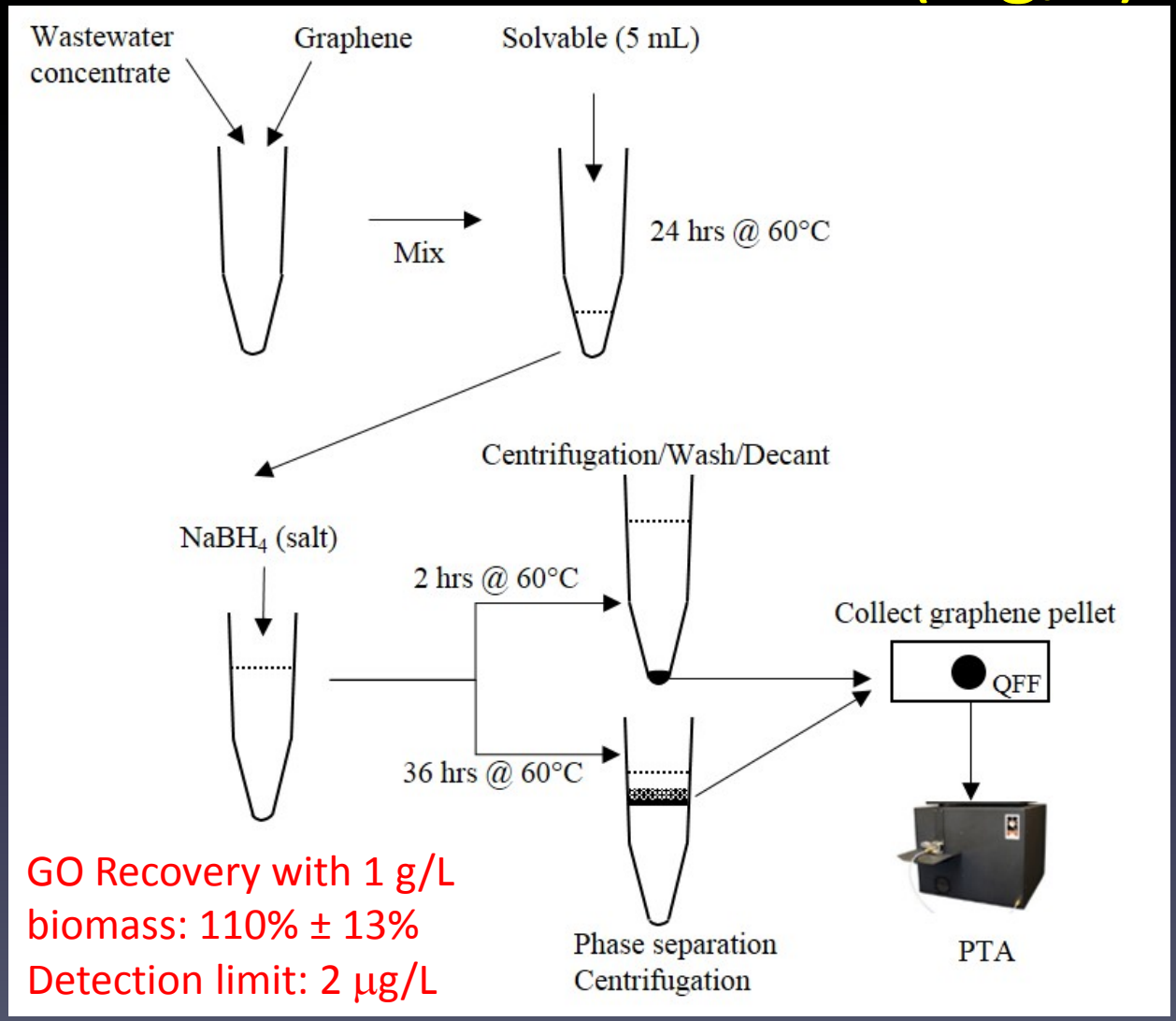


Step 3: Adding Solvable™ to degrade organics

- Solvable is an alkaline digestate that degrades organics; surfactant helps separation
- Solvable + $NaBH_4$ produces good pellet for separation & analysis



Final Digestion Method to Handle Separation of FLG, GO (or CNT) from High Biomass Concentrations (1 g/L)



GO Recovery with 1 g/L biomass: 110% ± 13%

Detection limit: 2 μg/L

Carbon NM Monitoring in Air Samples?

- Goal: To quantify the presence of CNTs in the presence of background air particulates
- Samples analyzed for organic carbon and CNT by PTA – which is a refinement to NIOSH Method 5040

Recovery of CNTs on air filter samples

(Conclusion: Excellent CNT recoveries indicates viability to monitor CNTs in workplace air)

Indoor air (MWCNT spiked onto filter)

Spiked CNT / ug	TOT data / ug
1	1.00±0.15
5	4.35±0.32
10	9.59±0.58

Outdoor air

Spiked CNT / ug	TOT data / ug
1	0.80±0.17
5	4.48±0.36
10	10.06±0.63

Conclusions

- C_{60} derivatives
  - Extraction in solvent (toluene) gives lowest detection limits using LC-MS
  - Solvent extraction from tissue and commercial products is possible
  - Extraction from urine and fluids can use solid phase extraction
- Graphene (FLG/GO) & CNTs (SW / MW)
  - Thermal methods can be non-selective unless related to known CNT or Raman analysis
  - spICP-MS emerging as potential indirect approach to quantify metal catalyst rather than carbon itself
  - Extraction from tissues aim to minimize oxygen incorporation => Alkaline conditions are better + Enzymatic digestion
- Personal monitoring devices can collect Carbon Materials and filters can readily be extracted for analysis