Carbon Nanotube Material Quality Assessment

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QUESTIONS

Why do we need material quality assessment?

What do we have to know?

How do we perform the characterization?

How much time and money can we spend?

How many times do we need to do?

What else do we have to know about the production source, i.e. laser, arc, CVD, etc.?

…….??????????

Material Quality = Purity?

Why Do We Want to Know Nanotube Purity?

- Over the years, various manufacturers claimed purity anywhere from 50 to 90%. Do we trust these numbers? What are we buying?

- How consistent is NT material produced by the same manufacturer in different batches?

- What are implications of nanotube purity in applications?

- How does the purity affect stress transfer in composites, electrical and thermal conductivity, surface area, sidewall chemistry, dispersion properties, etc.?

What do We Really Like to Know?

Morphology	Purity	Dimensionality	Physical Properties	Chemical Interaction & Modifications
Physical Shape	Density	Lengths	Thermal	Dispersion
Texture	Metal Impurity	Diameters	Electrical	Functionality
Color/Shade/Tint	Carbon Impurity	Chirality	Mechanical	Defects
Homogeneity	Other Impurities	Surface Area	Magnetic	Exfoliation
Surface Features	Residual Mass	Pore Size	Optical	
Fiber Types				
Impurity Features				

How do We Perform Characterization?

Macroscopic

- **Thermal Gravimetric Analysis (TGA)**
- **UV-Visible-Near Infrared (UV-Vis-NIR) Absorption**
- NIR Fluorescence
- Inductively Coupled Plasma (ICP)
- Optical Microscopy
- Dynamic Light Scattering (DLS)
- X-ray Diffraction (XRD), SAXS, SANS
- Resistivity
- Surface Area(BET)
- Tensile Strength
- Thermal Conductivity

Microscopic

- **Scanning Electron Microscopy (SEM)**
- **Energy Dispersive X-ray Analysis (EDX)**
- **Raman Spectroscopy**
- X-ray Photoelectron Spectroscopy (XPS)

Nanoscopic

- **Transmission Electron Microscopy (TEM)**
- Atomic Force Microscopy (AFM)
- Scanning Tunneling Microscopy (STM)

Purity and Dispersion

Our goals for Quality Assessment*

- To be able to directly compare nanotube samples of different origin, purified by different techniques.
- To gather as much information as possible about specimen purity (non-nanotube carbon impurities and metal content), dispersability and homogeneity.
- To minimize time and effort spent on characterization.
- To optimize data collection to provide reliable assessment.

Available tools:

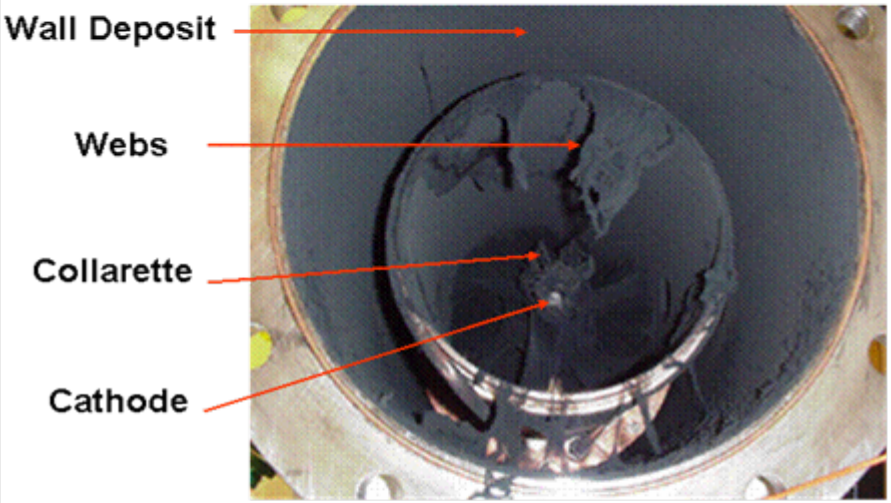
- Thermogravimetric analysis (TGA), (TA SDT 2960)
- Transmission electron microscopy (TEM) + EDS, (JEOL 2010 FX)
- Scanning electron microscopy (SEM) +EDS (Phillips XL40 FEG)
- Raman spectroscopy (Renishaw RM 1000)
- UV-Visible spectrometry (Perkin-Elmer Lambda 900)

* Ref: "NASA-JSC Protocol"; Carbon, Vol. 42, pp. 1783-1791 (2004)

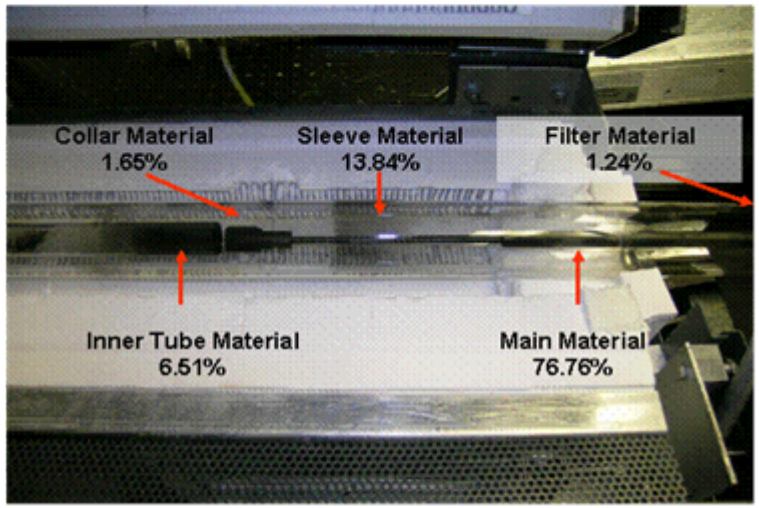
How does the material vary with production source?

Production and Collection

Arc Discharge Method



Pulsed Laser Vaporization



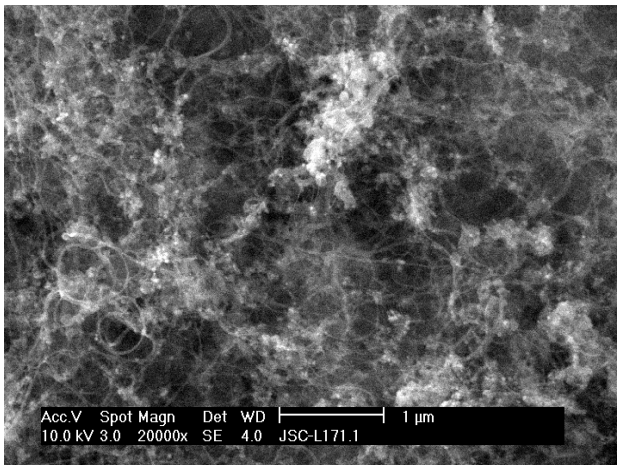
Arc Production Conditions:

3.92%Ni:1%Y, Pressure:506 Torr, Voltage:38.2V, Current:101.5A, Electrode Distance:3 mm, Automated

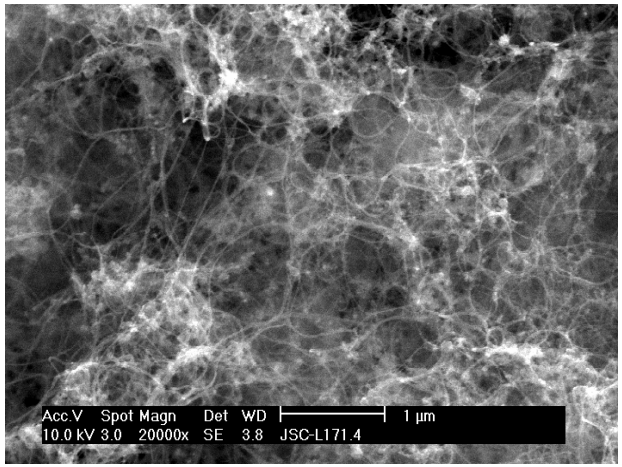
Laser Production Conditions:

¾" diameter target, 1%Co:1%Ni, Pressure: 500T, Ar Flow Rate: 100 sccm, Pulse Separation: 50 ns , Power Density: 1.6J/cm^2, Oven Temperature: 1200 ^{o}C, Laser Sequence: Green-IR

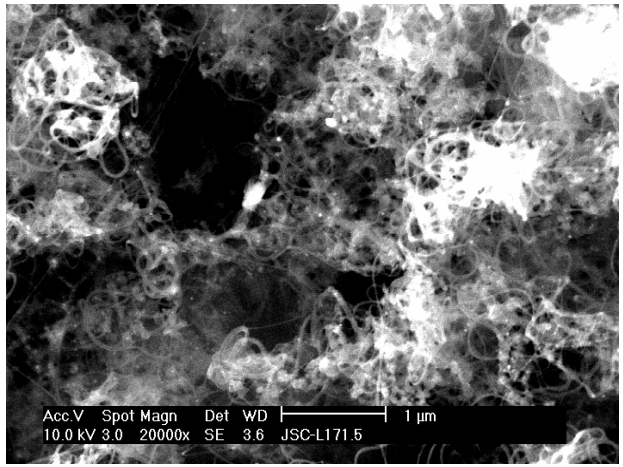
Laser Run #171; Morphology



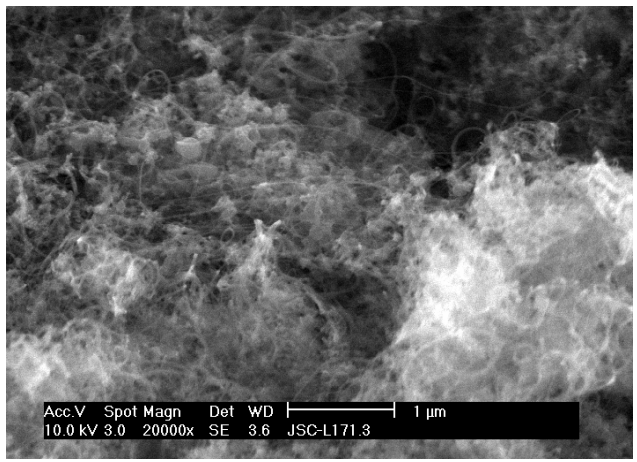
Collar



Sleeve



Main Material



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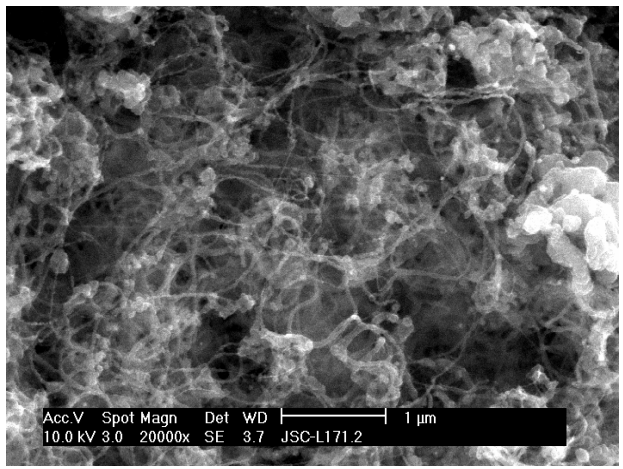
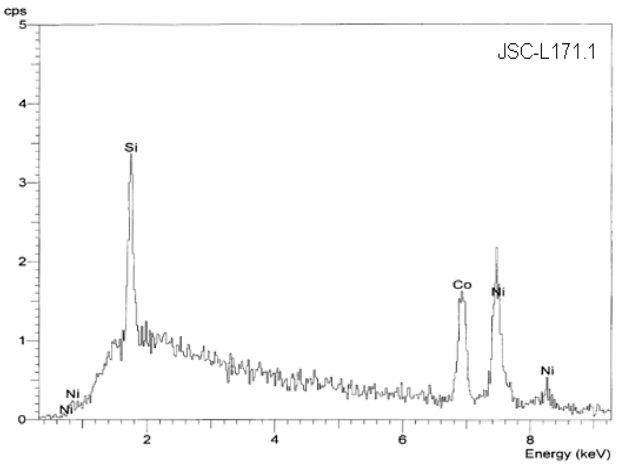


Inner Flow Tube

Laser Run #171; Purity by EDX



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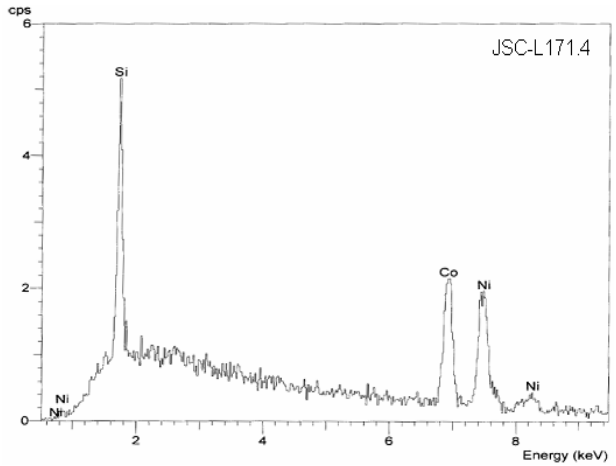

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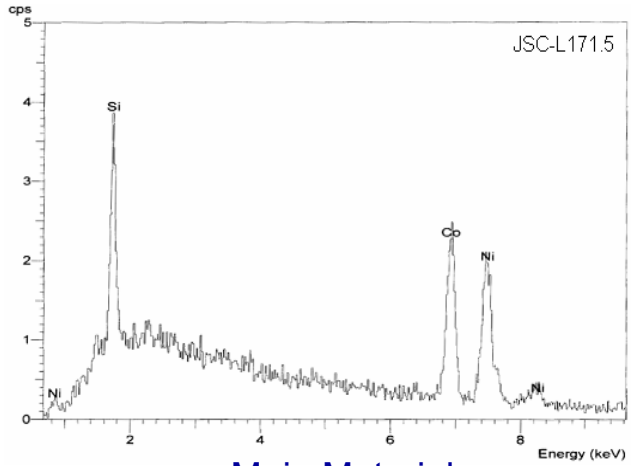
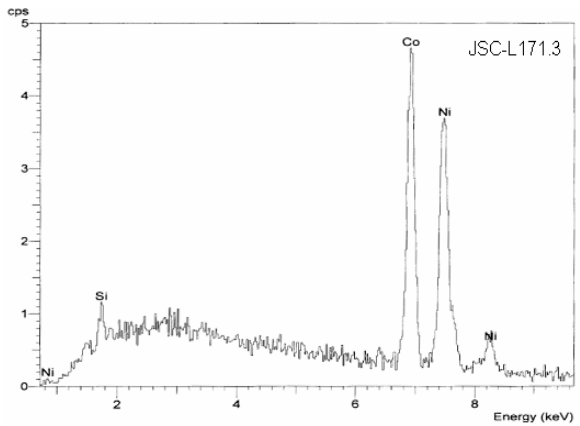


Main Material



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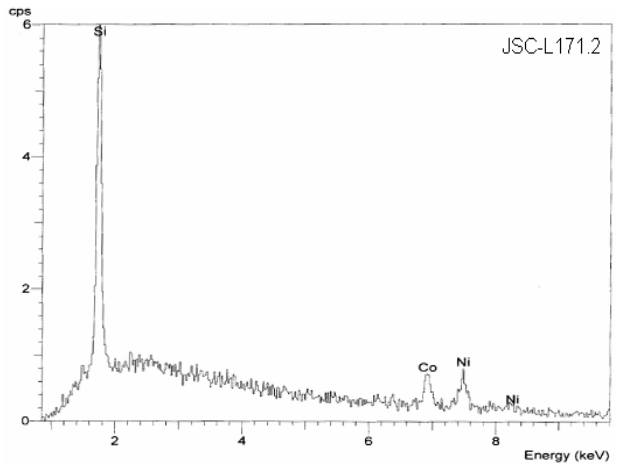
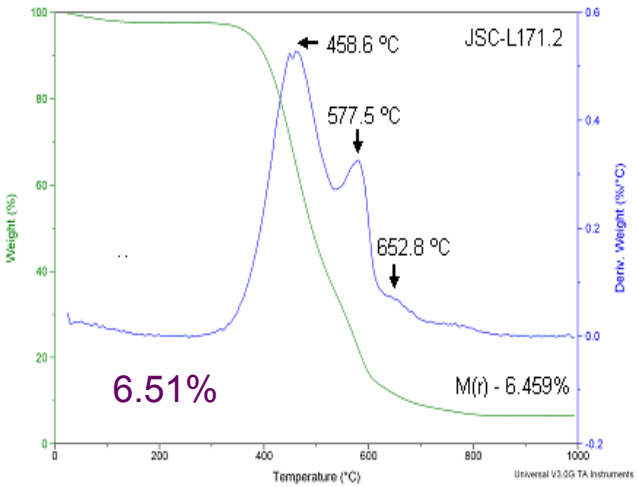
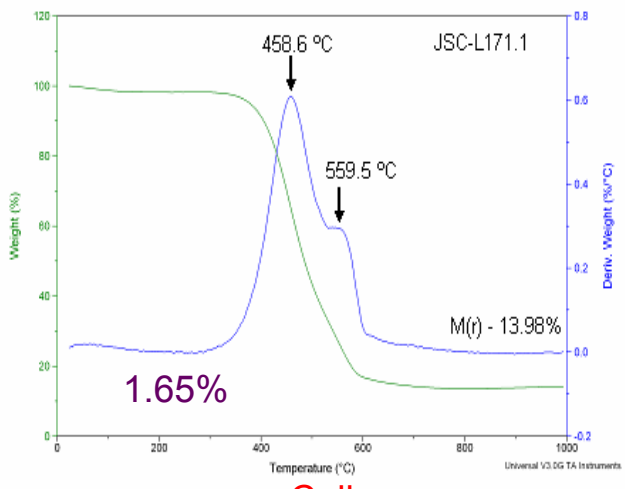


Inner Flow Tube

TGA Harvesting Characterization



Inner Flow Tube



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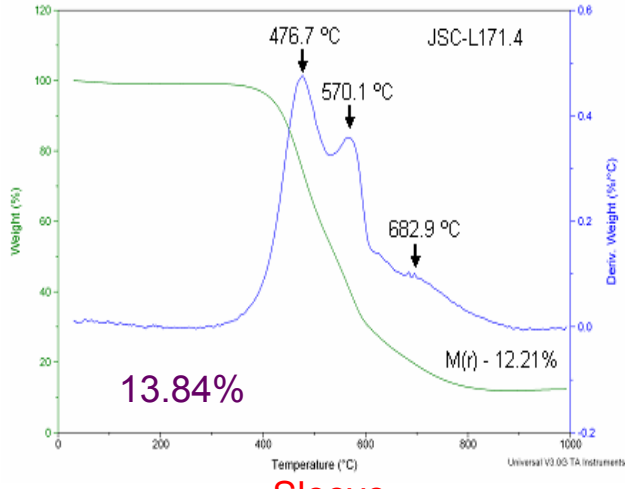
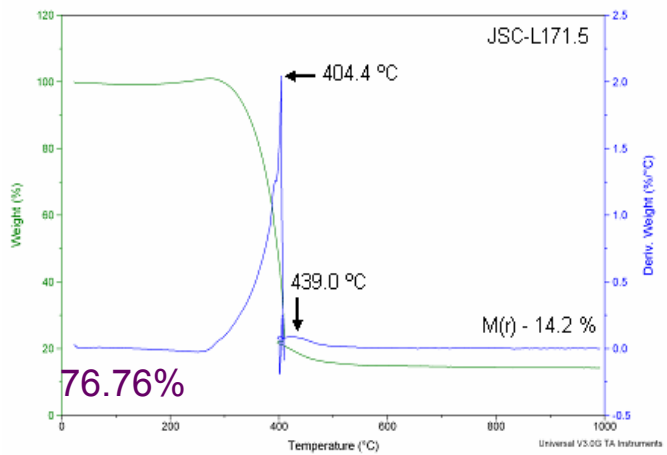
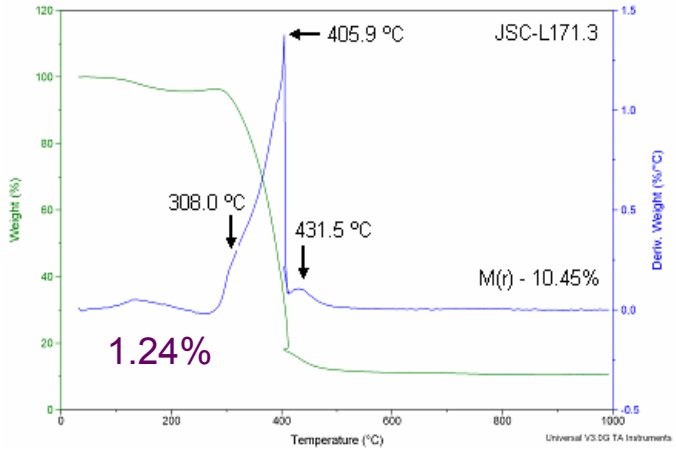


Sleeve



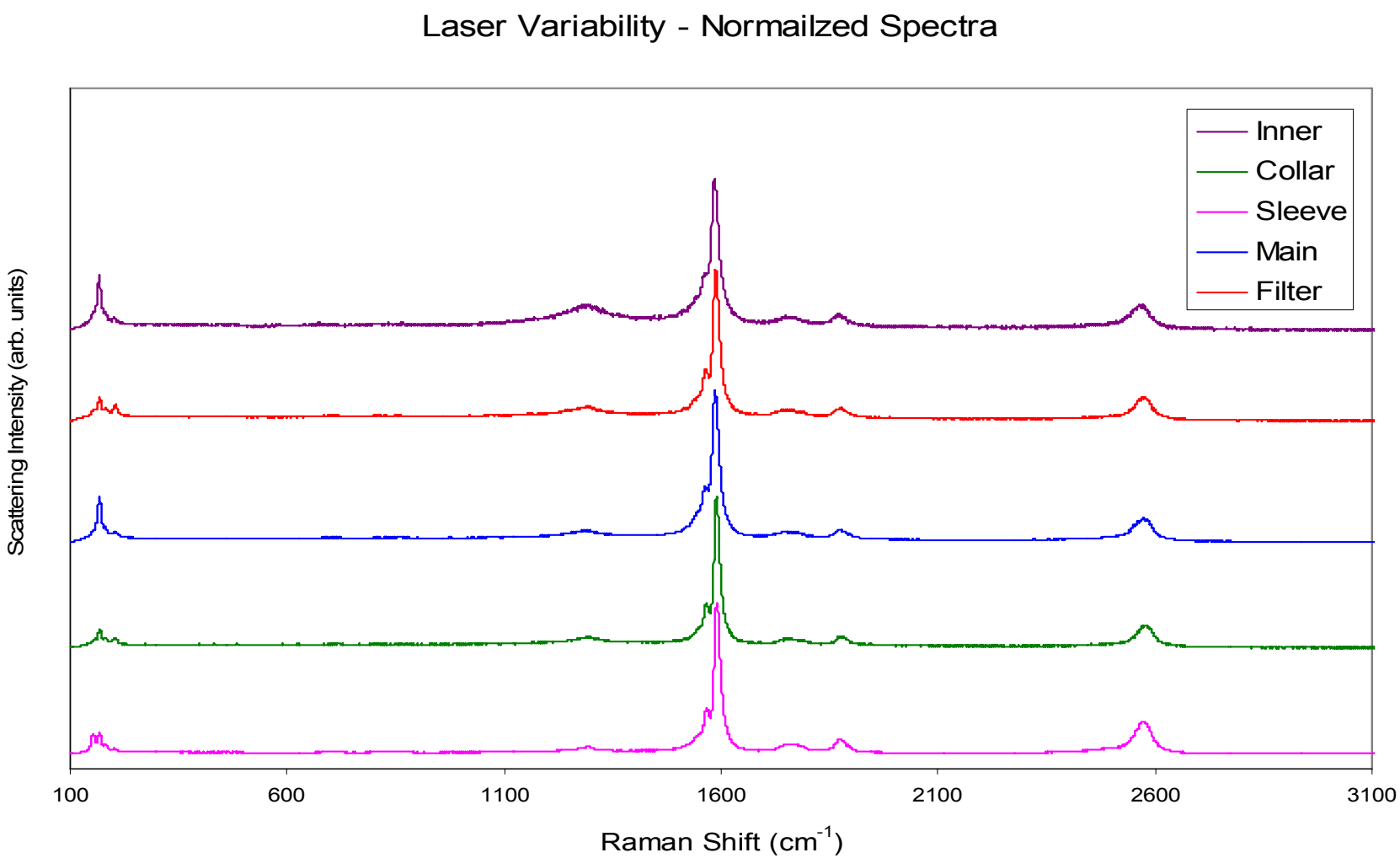
Main Material



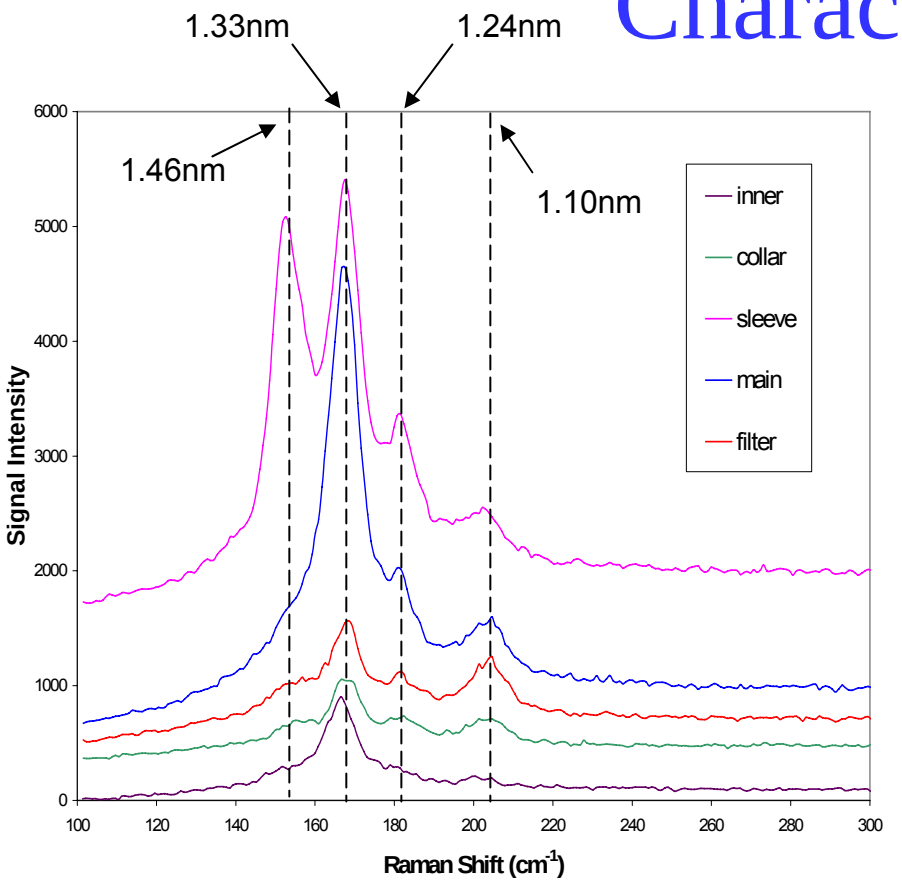
Filter

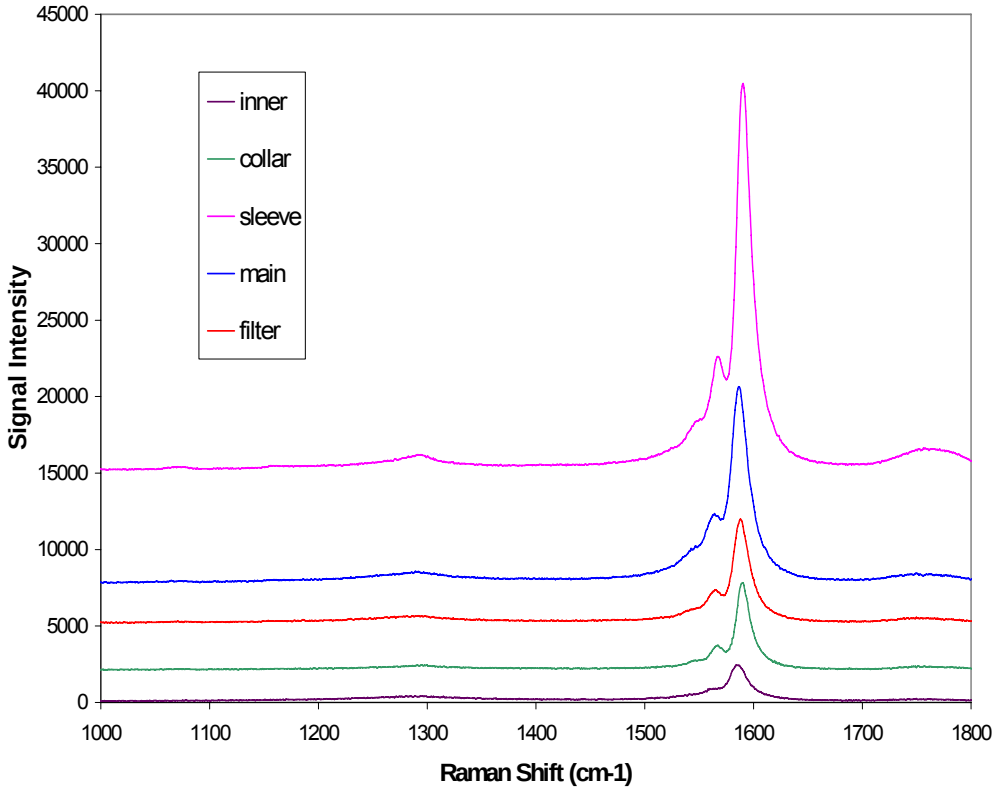
∗ Indicates the percentage of material weight collected ∗

Raman Spectroscopy Harvesting Characterization



Raman Spectroscopy Harvesting Characterization

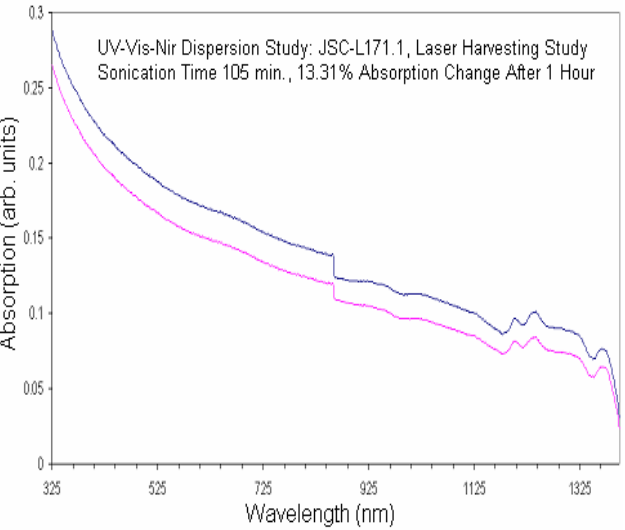




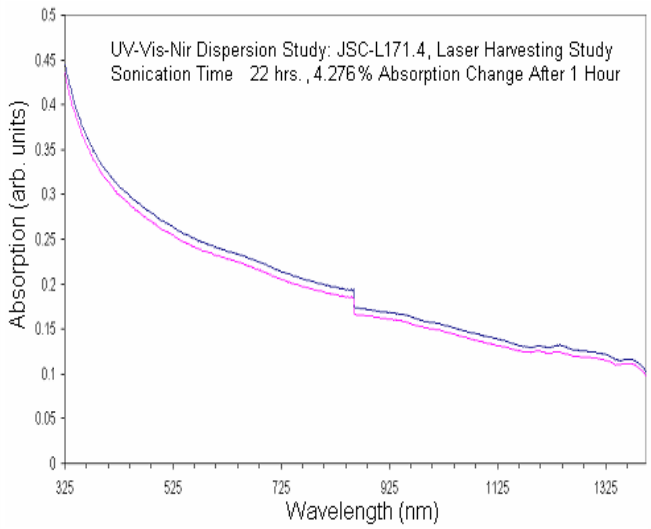
$\omega_{RBM} = \alpha/d + b$, α = constant = 223.5 cm^{-1}• nm

b = intertube interactions = 12.5 cm^{-1}

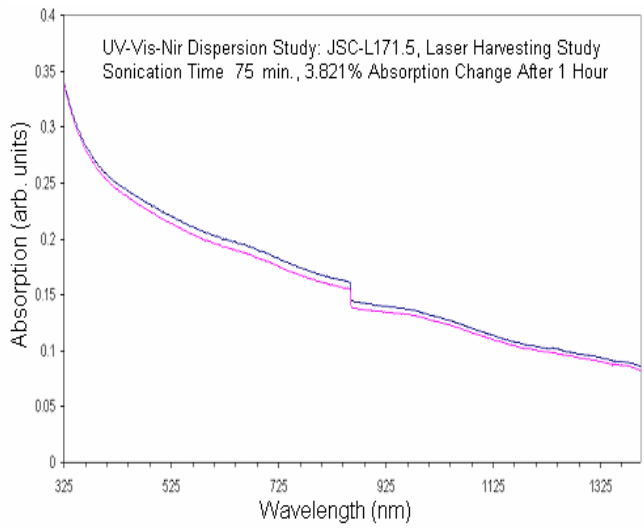
Laser Run #171; Purity and Dispersion by UV-Vis-NIR Spectroscopy



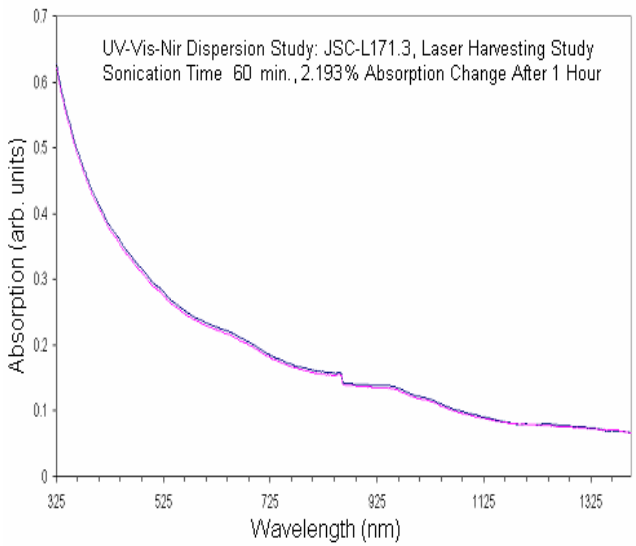
Collar



Sleeve



Main



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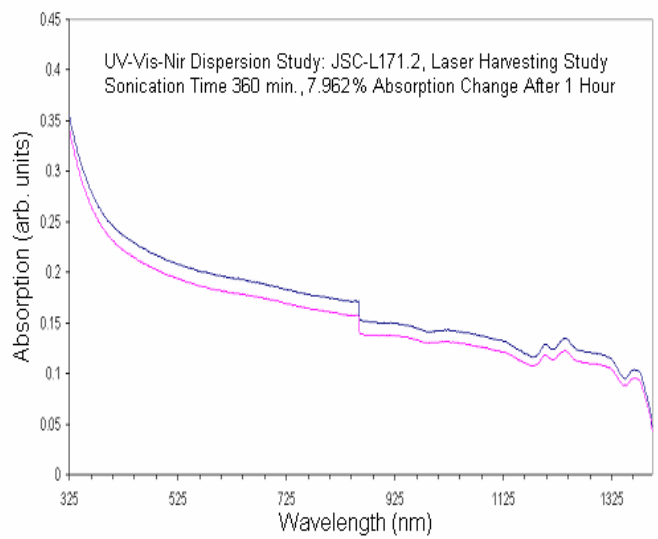


Inner Flow Tube

Laser Collection Variability Summary

MATERIAL

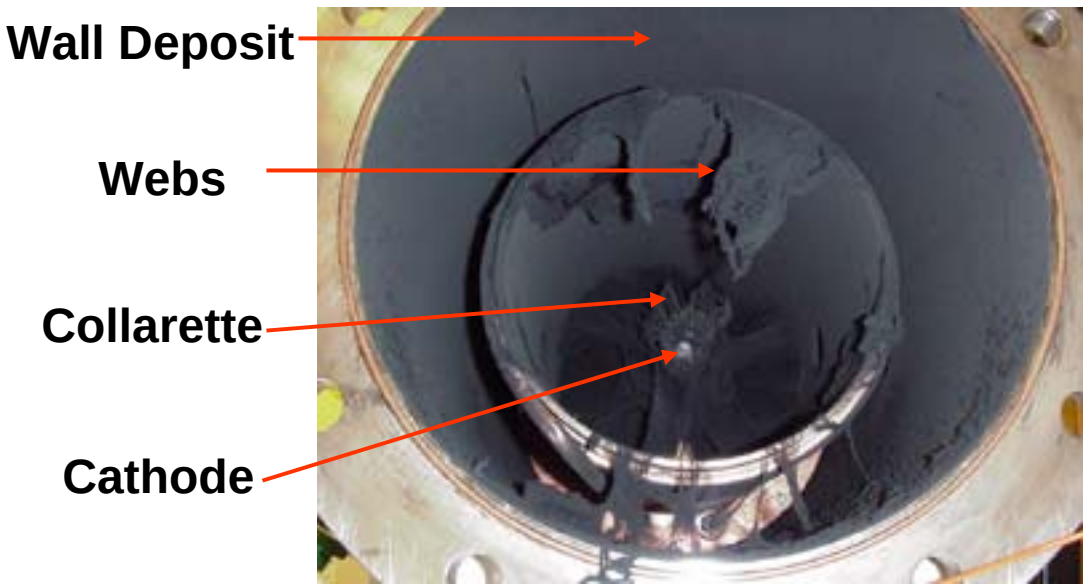
PROPERTIES	Inner	Collar	Sleeve	Main	Filter
Residual Mass	6.45%	13.98%	12.21%	14.26%	10.45%
Thermal Stability	Min 458.6 ºC Max 652.8 ºC	Min 458.6 º C Max 559.5 º C	Min 476.7 º C Max 682.9 º C	Min 404.4 º C Max 439.0 º C	Min 405.9 º C Max 431.5 º C
Dispersion	7.962%	13.31%	4.276%	3.821%	2.193%
D/G Ratios	0.288	0.090	0.047	0.094	0.124
D-Band Position	1285.45cm^{-1}	1289.9cm^{-1}	1287.87cm^{-1}	1284.84cm^{-1}	1283.17cm^{-1}
Small Diameter %	8.02%	22.6%	8.17%	9.85%	27.5%

Conclusions

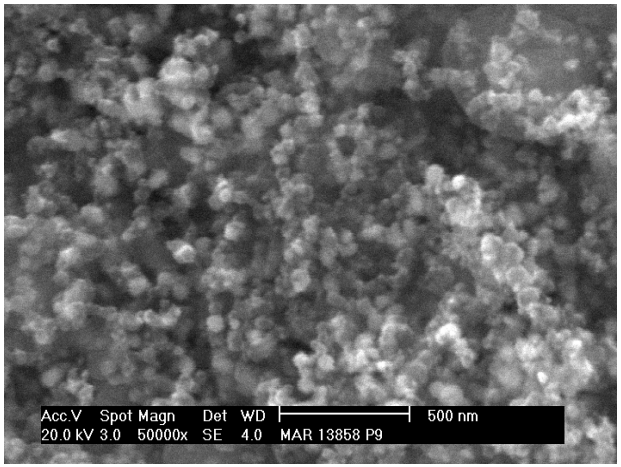
- Downstream SWCNT material tends to have lower thermal stability
- TGA spectral shape similar for main and filter SWCNT material. Inner tube material has half the residual mass compared to other materials.
- Downstream material is less crystalline (?) and more fluffy (TGA and UV-Vis-NIR)
- Spectral features in UV-Vis-NIR data is directly proportional to distance from target
- Percent Absorption change is inversely proportional to distance from target

Variability Study of Harvested Arc Material

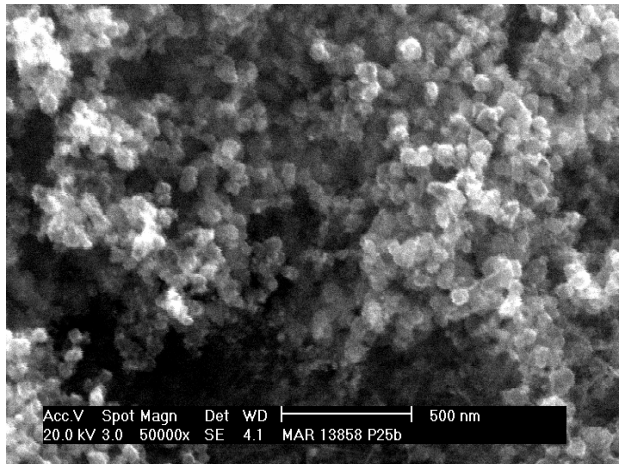
- Harvested Arc Material deposited on the cathode, collarette, webs and chamber wall.
- Characterized using JSC Protocol for SEM, TGA, UV-Vis and Raman



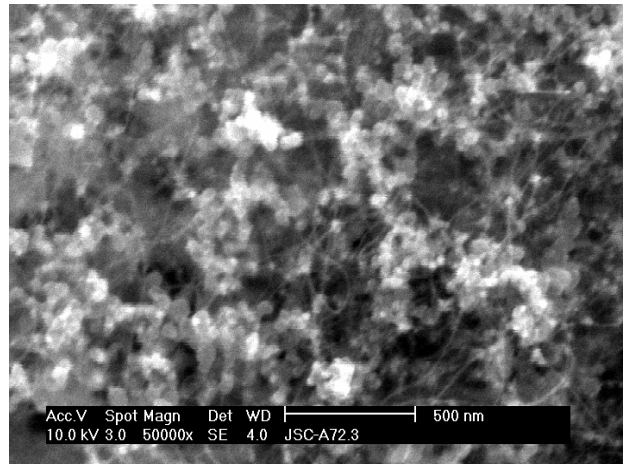
Variability Study of Harvested Arc Material



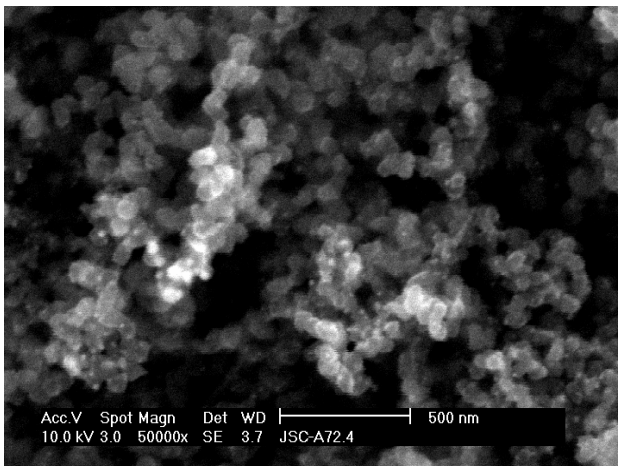
Cathode (JSC-A72.2)



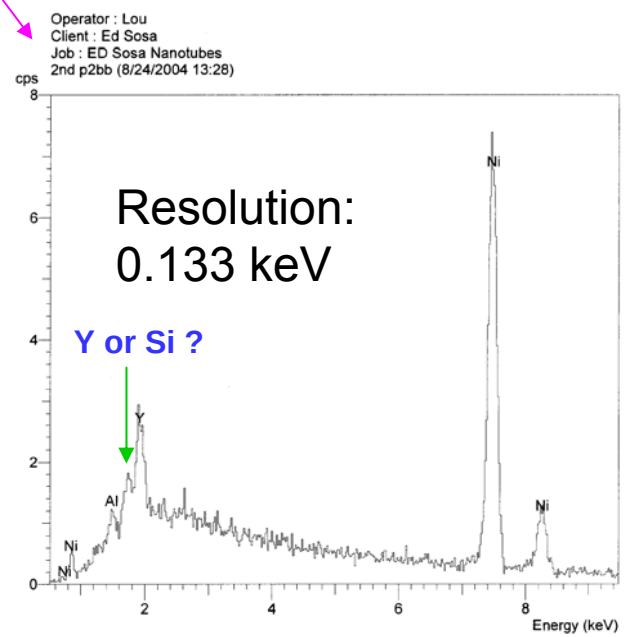
Collarette (JSC-A72.1)

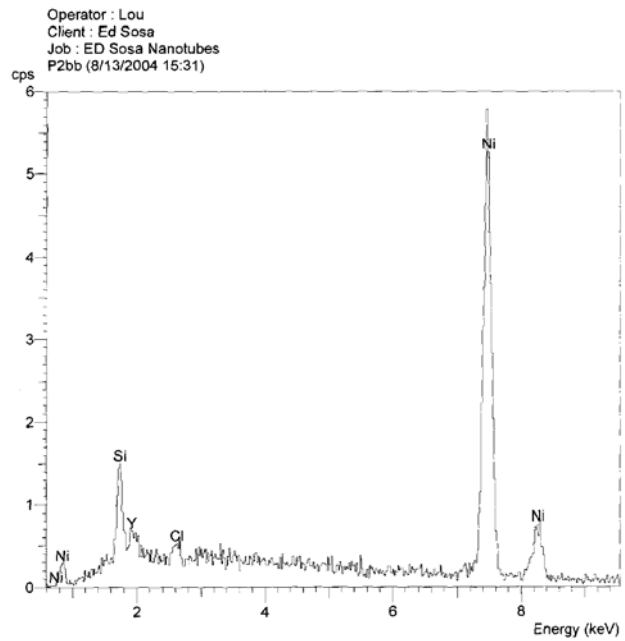


Webs (JSC-A72.3)

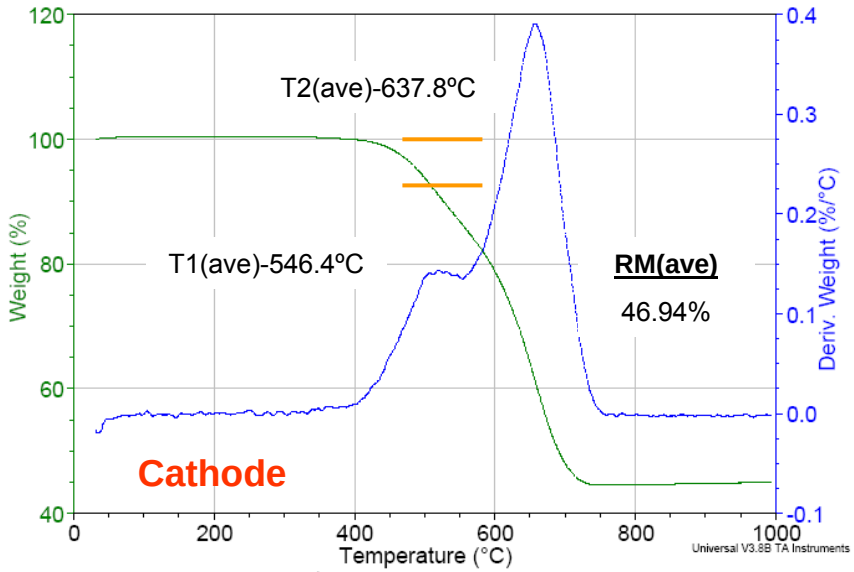


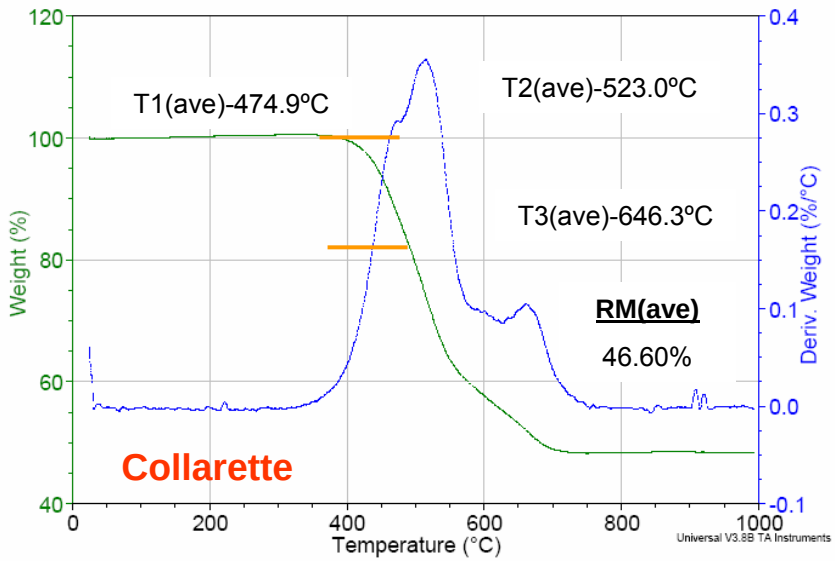
Wall Deposit (JSC-A72.4)

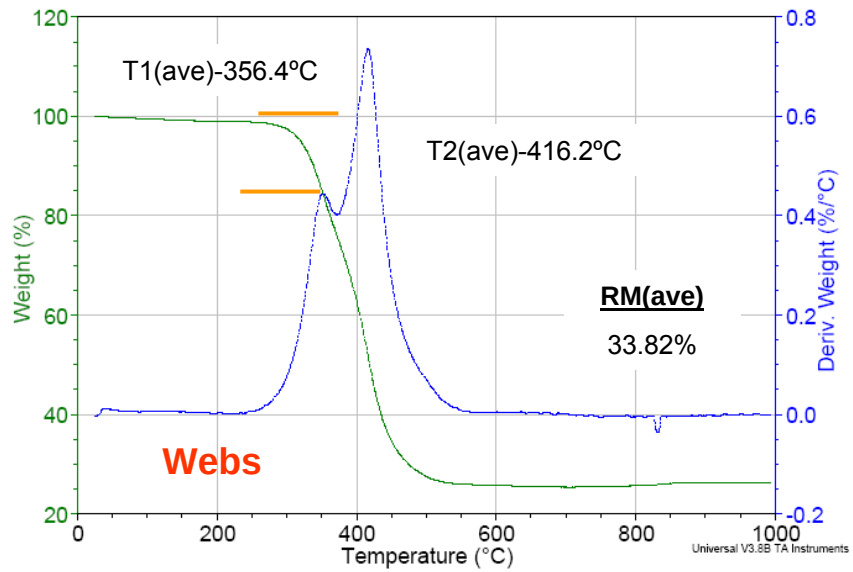


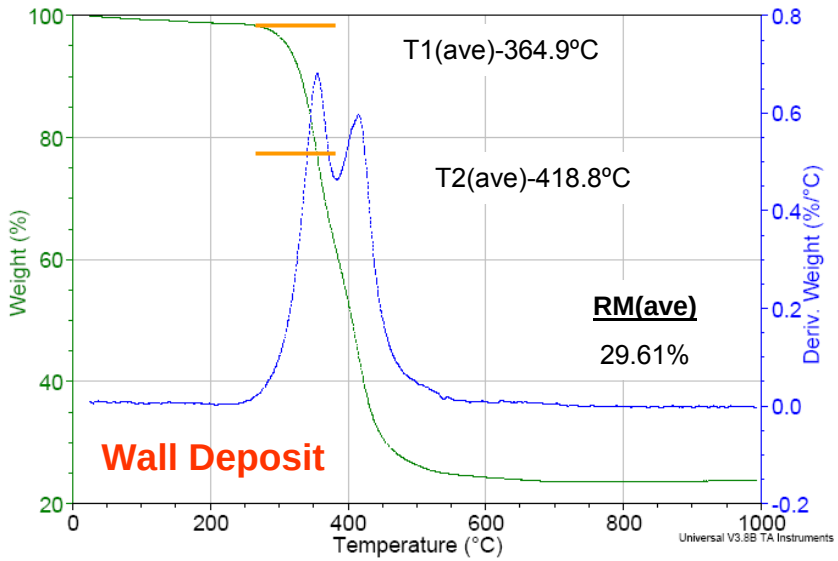


Variability Study of Harvested Arc Material



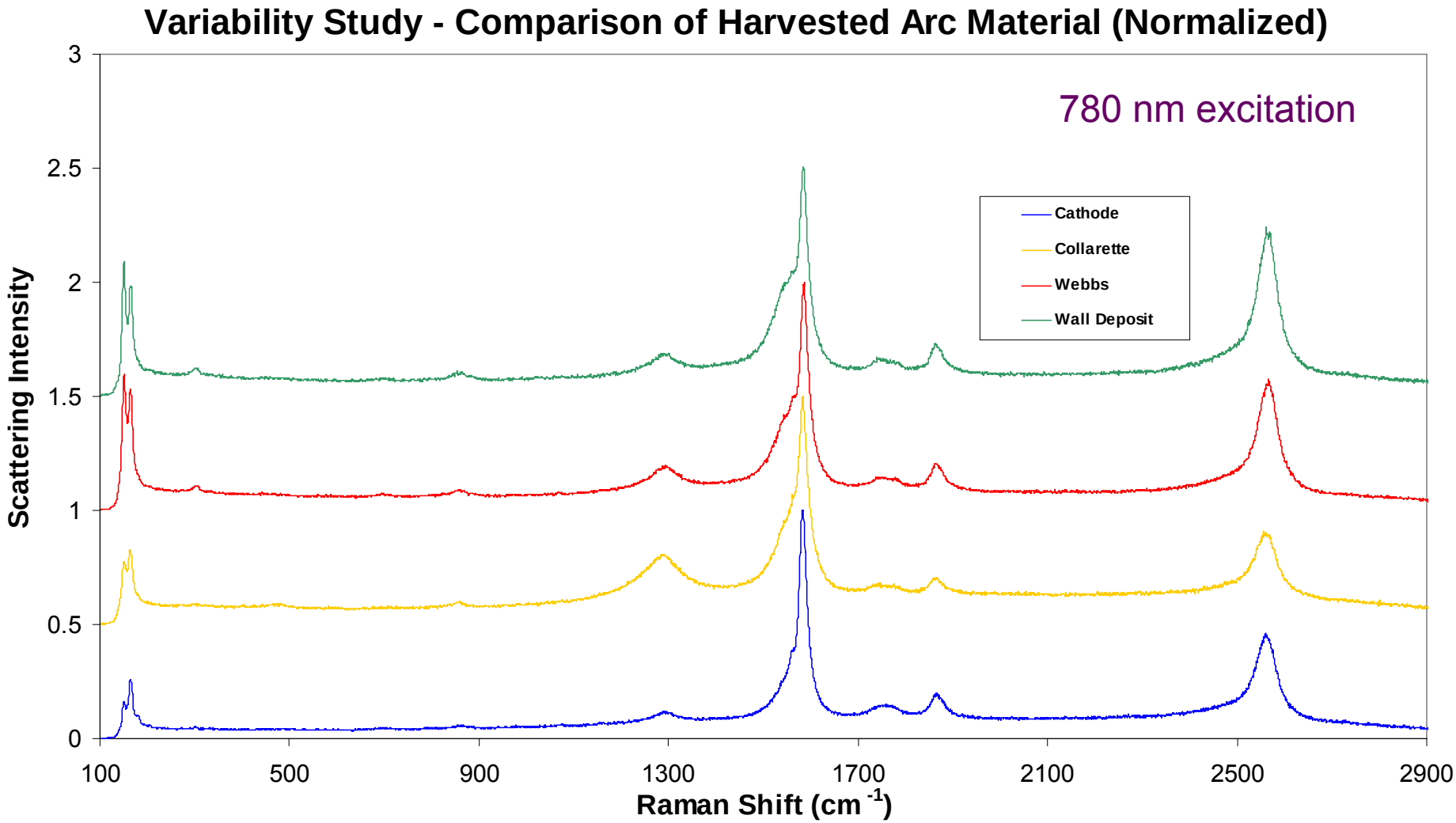




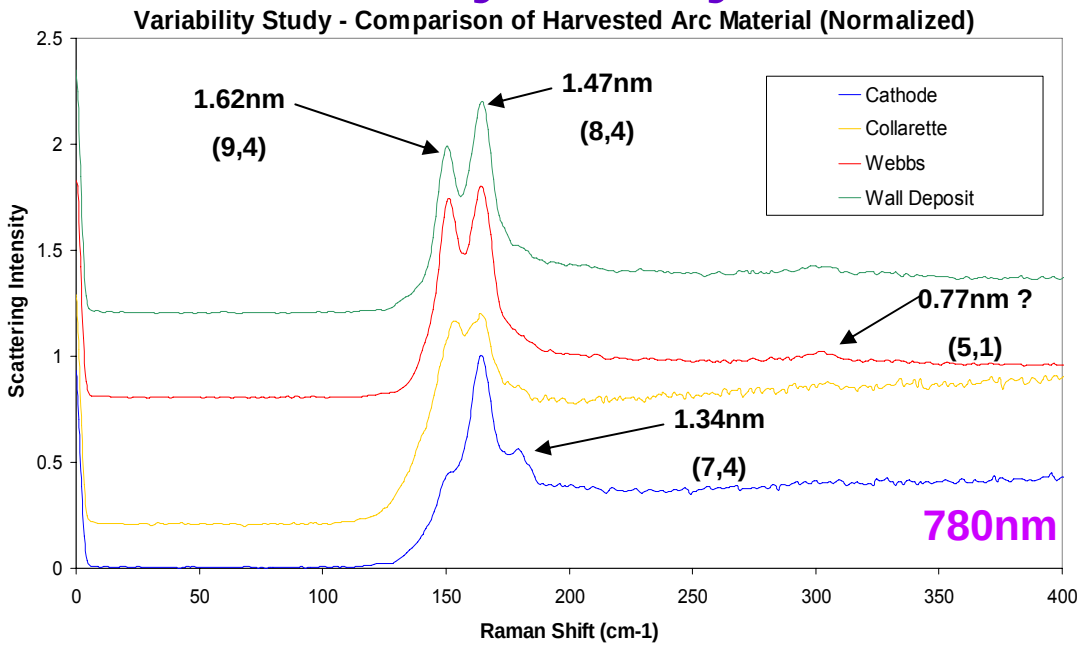


Possible causes for the variation: 1. Over-coating of metals 2. Tube diameters

Variability Study of Harvested Arc Material

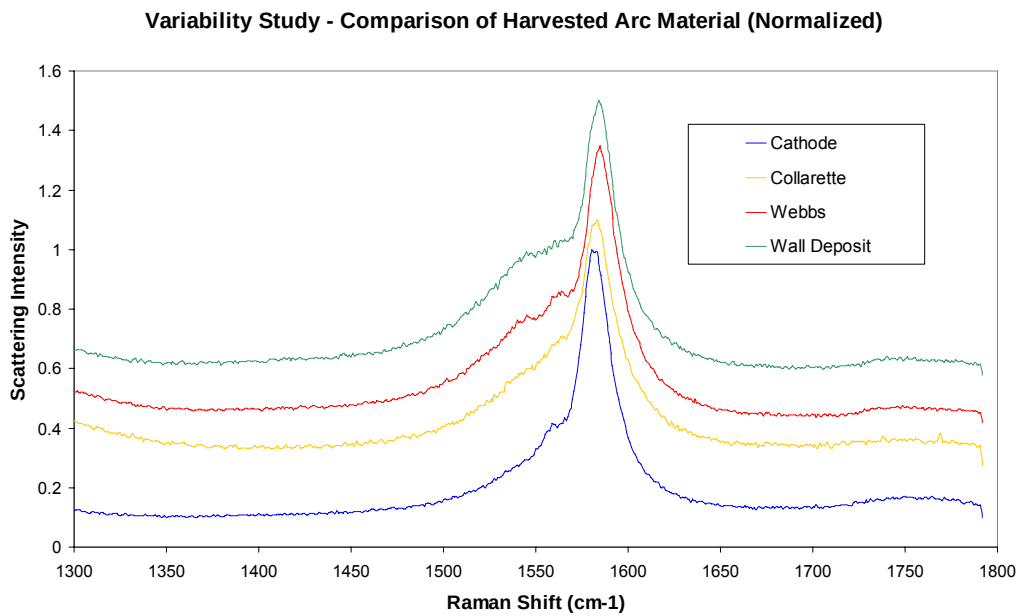


Variability Study of Harvested Arc Material



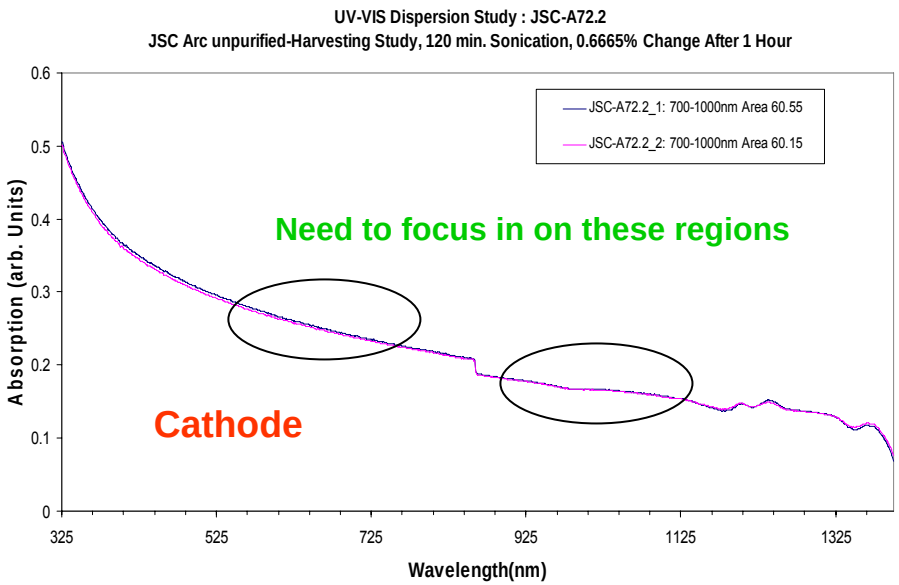
Material deposited further away from electrodes have larger contribution of larger diameter tubes.

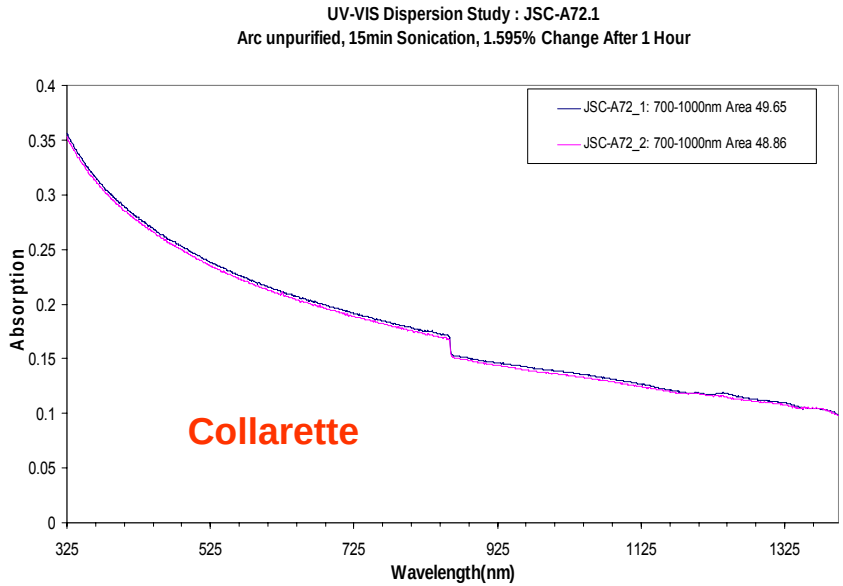
$D_{web} > D_{wall} > D_{col} > D_{cat}$

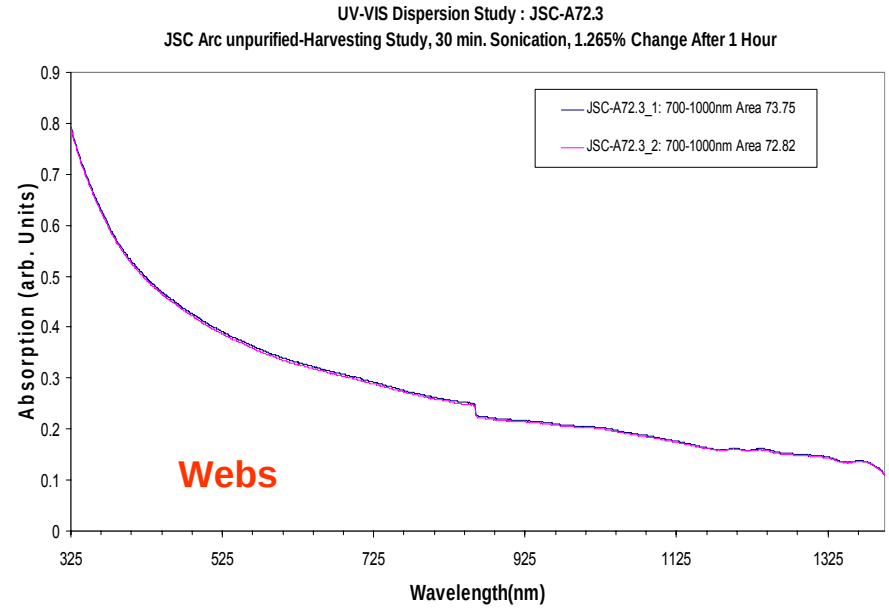


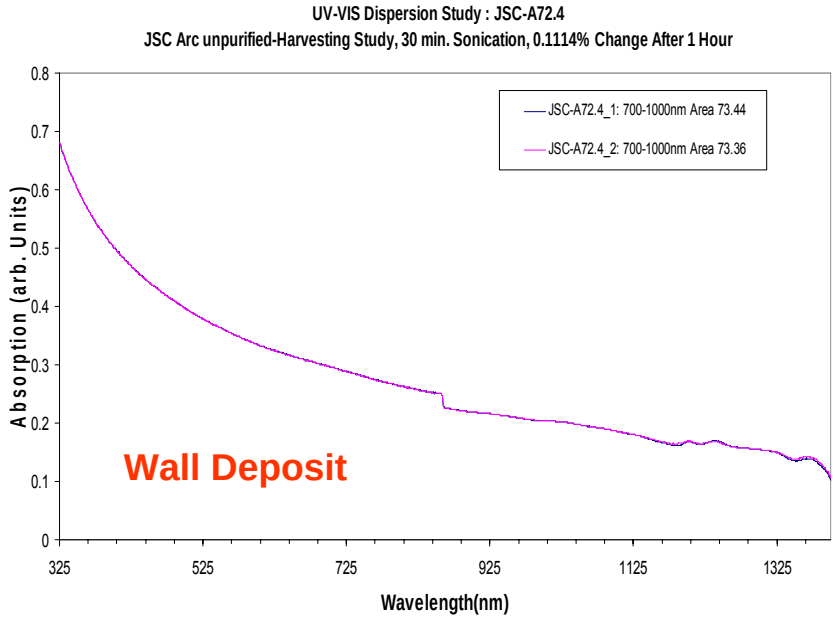
G-band agrees with diameter fractions – webs and wall deposit have higher fraction of larger diameters.

Variability Study of Harvested Arc Material









Arc Collection Variability Summary

Arc Material:

Properties	Collection Region: Cathode	Collarette	Webs	Wall Deposit
Residual Mass (ave)	46.95%	46.60%	33.82%	29.61%
Thermal Stability (ave)	Min 458.8 °C Max 637.8 °C	Min 474.9 °C Max 646.6 °C	Min 356.4 °C Max 416.2 °C	Min 364.9 °C Max 418.8 °C
Dispersion	0.6665%	1.595%	1.265%	0.114%
D/G Ratios	0.0337	0.1655	0.0873	0.0438
Small Diameter % (Raman)	20.9%	8.87%	5.39%	4.97%

Conclusions

TGA:

Lower oxidation temps for material further from electrodes more likely due to some degree of over-coating.

Lower metal content observed inversely to distance from electrodes.

Raman:

D-band does not support TGA carbon impurity speculation.

RBM suggests smaller diameters more prevalent in cathode materials.

G-band may show more metallic features in cathode material, while more SC features in wall deposit.

UV-Vis:

Suppressed optical features support over-coating of tubes.

Stronger S22 transition in agreement with Raman results.

Thanks for Your Attention