"Purity measurements and purity standard of single-wall carbon nanotubes"

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Purity and Dispersion Part II
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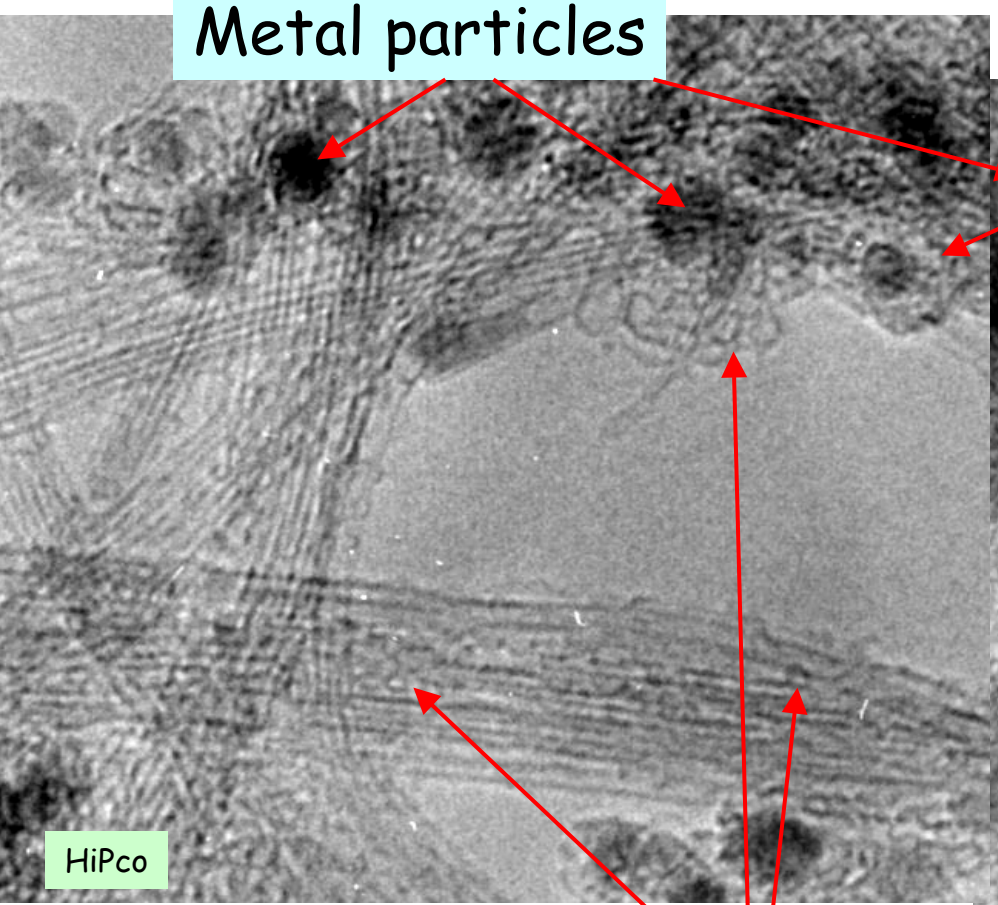
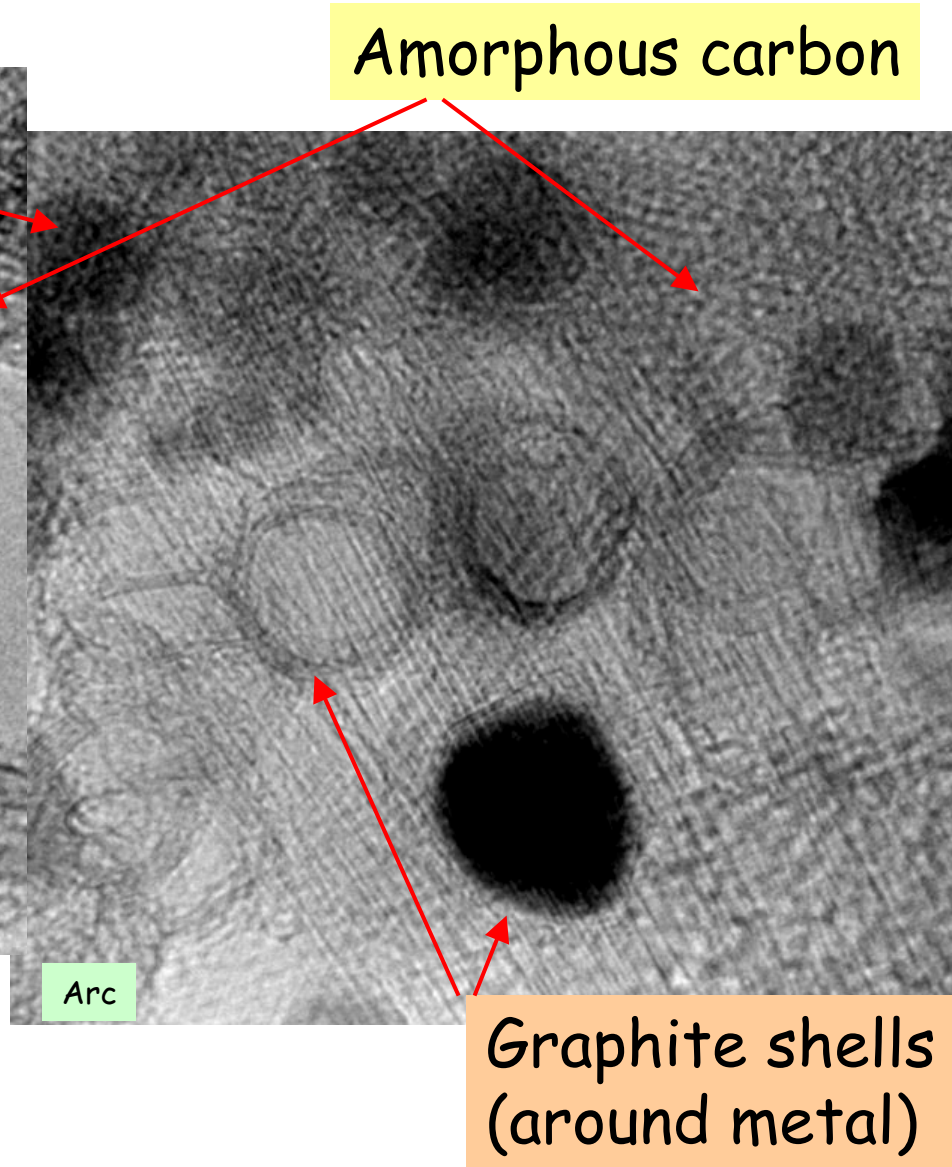
Known impurities in single-wall carbon nanotubes





Why do we want to know nanotube purity?

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

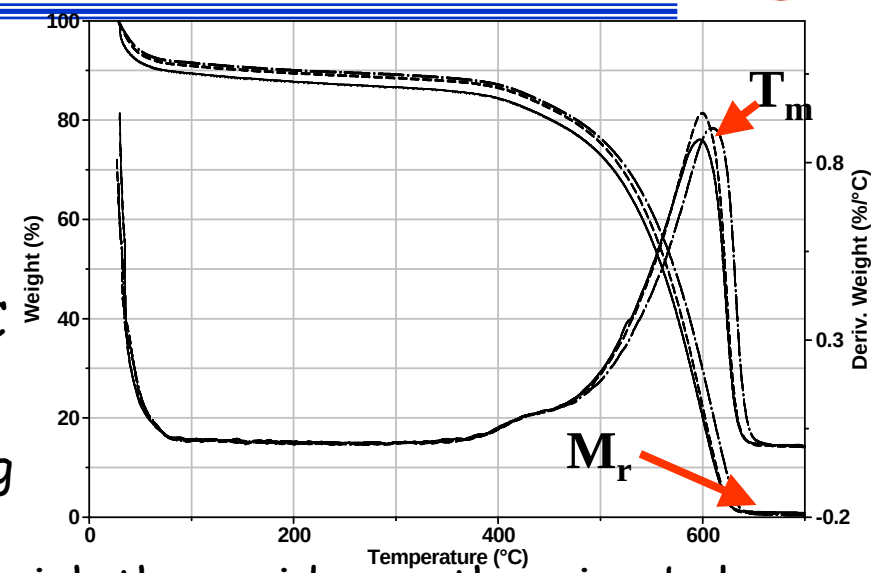
- How consistent is NT material produced by the same manufacturer in different batches?

- What are implications of nanotube purity in applications? How does it affect stress transfer in composites, electrical and thermal conductivity, surface area, sidewall chemistry, dispersion properties, etc.?

Metal content

Can be easily determined as a residue in TGA

- 3 runs on 3-4 mg of material
- Conditions: 100 sccm air, 5 °C/min heating rate, room temperature to 800°C
- Each run takes ~3 hrs. Apparently, baseline instability of TGA exceeds 10 μg over this time span. Therefore it is necessary to weigh the residue on the microbalance after each run and correct results accordingly.



•Information extracted from TGA data (JSC protocol):

1. Average residual mass M_r (in %): Shows **fraction of residual metals** in the specimen.

2. Temperature T_m of the maximum in the burning rate dm/dT : Shows **thermal stability** of the specimen.

3. Standard deviation of M_r and T_m: Shows **homogeneity** of the specimen

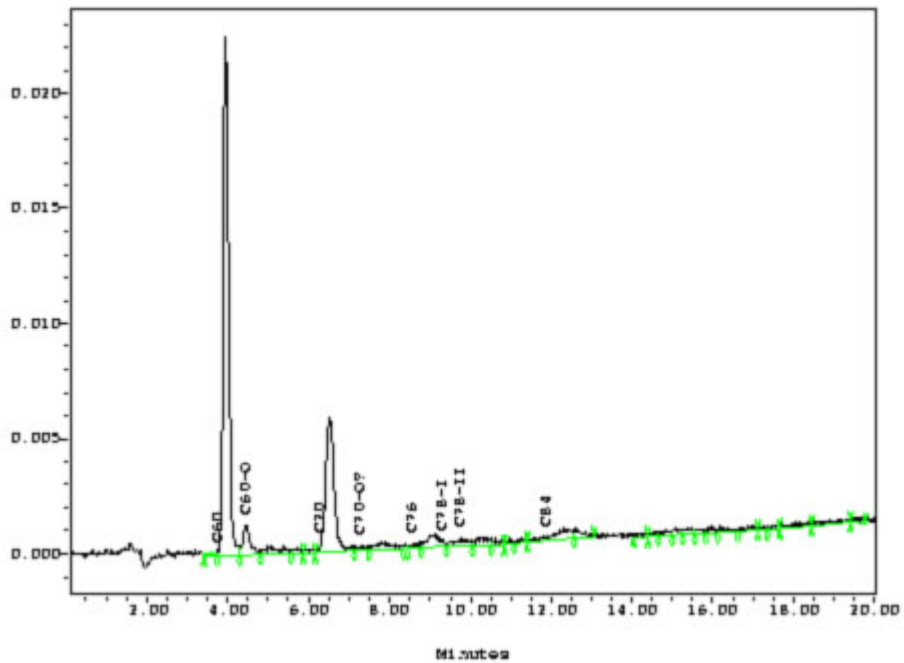
Fullerene content

- Can be determined by toluene extraction followed by HPLC (high-performance liquid chromatography)

- Not a serious problem - ~2-5% in laser NT, <<1% in HiPco NT

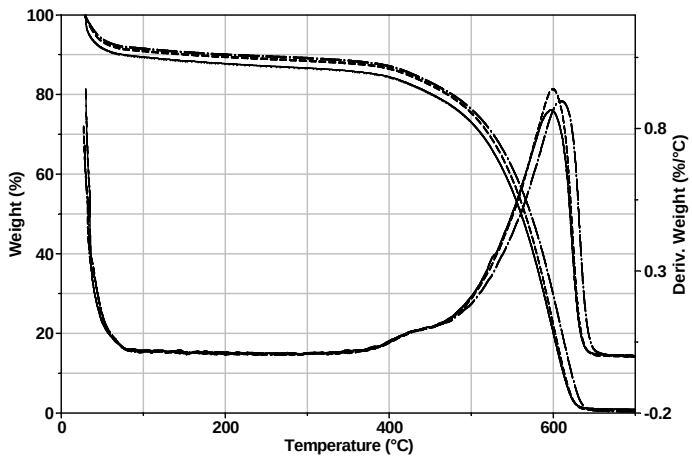
- We usually extract fullerenes from laser NT with toluene before purification, and ignore them in HiPco NT

- Fullerenes are never found in purified NT

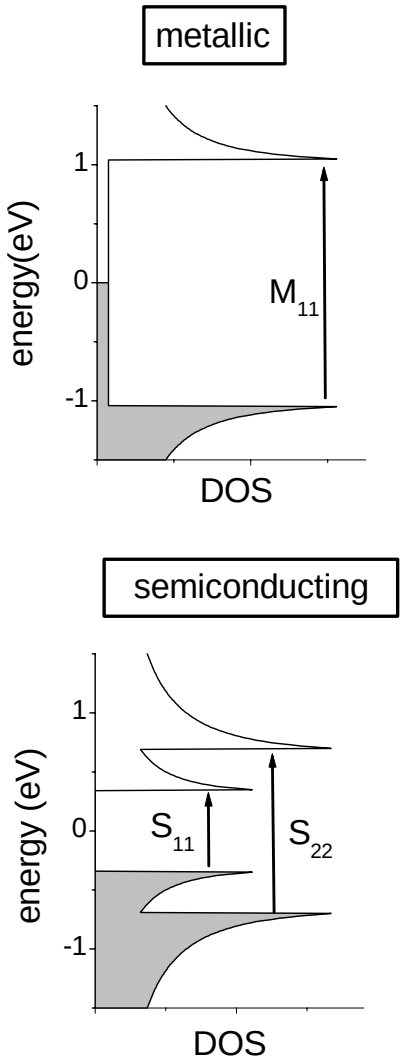


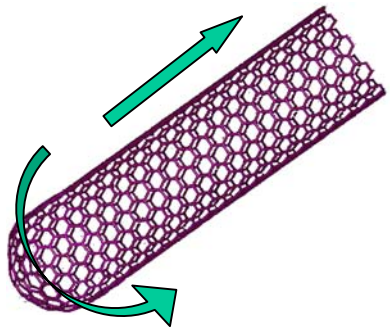
Amorphous carbon and graphite (non-tubular carbon impurities)

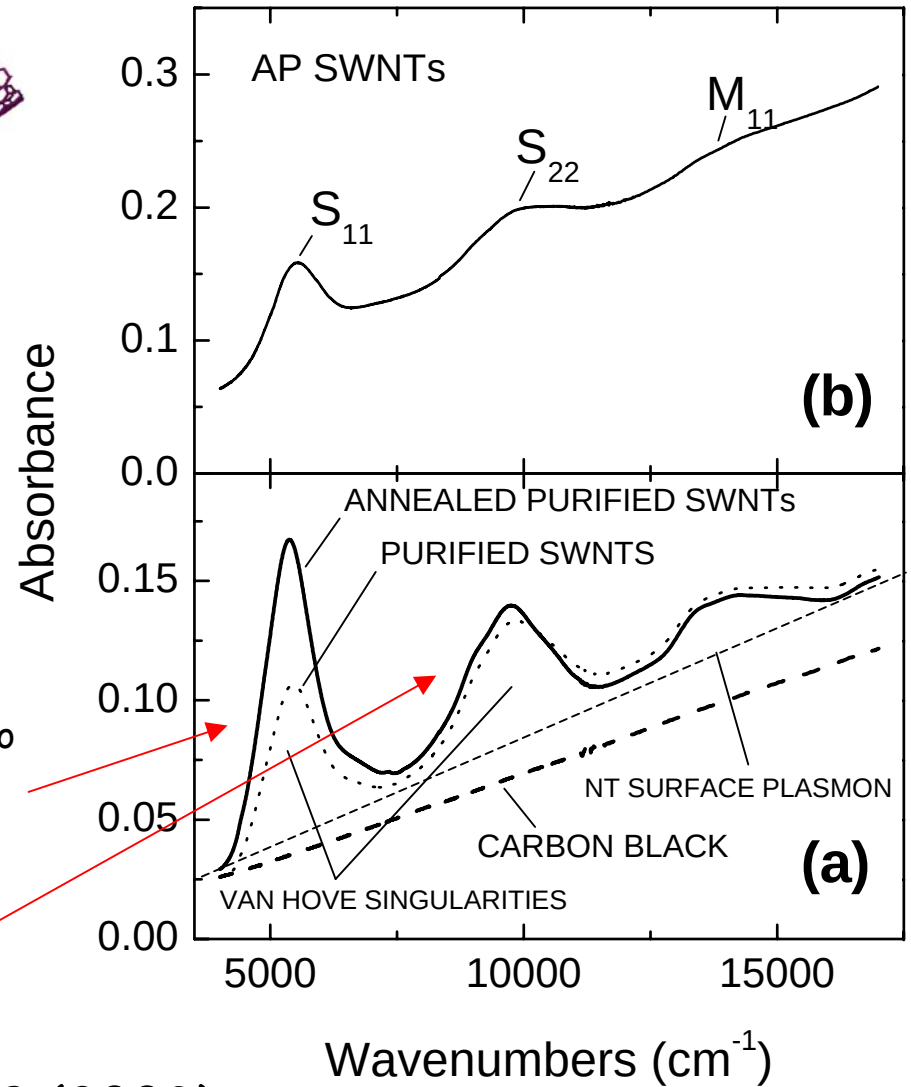
- No simple analytical technique can easily distinguish various forms of sp^2 carbons
- Microscopy is very subjective
- TGA in air does not work – NT, amorphous carbon and graphite oxidation overlaps too much
- **Spectroscopy?**



How can we measure the non-tubular carbon impurities?





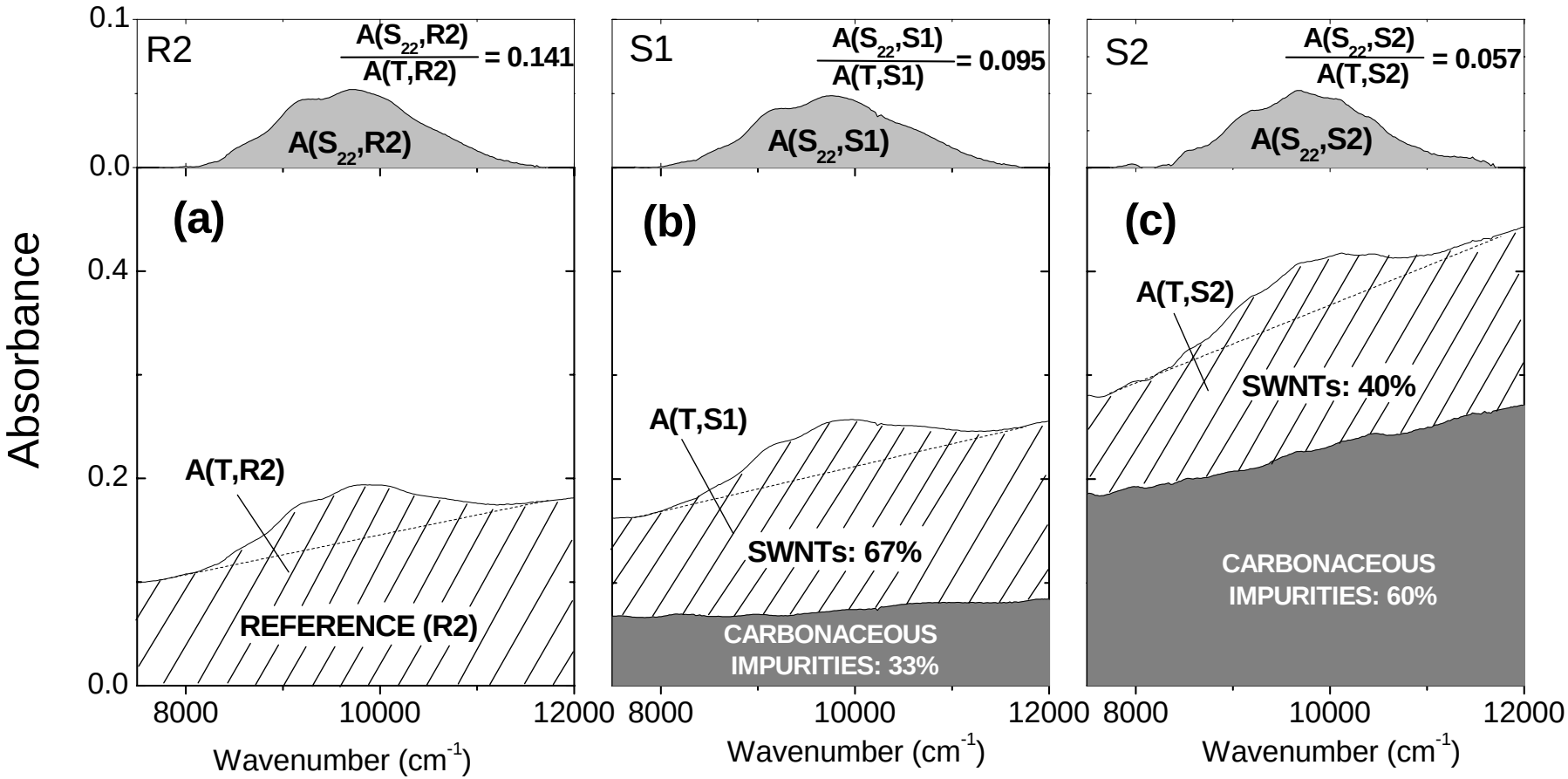


S_{11} is sensitive to derivatization, protonation, solvents, etc.

S_{22} is not !

M. E. Itkis, et al. Nano Lett, **3**, 309 (2003)

How can we measure the non-tubular carbon impurities?



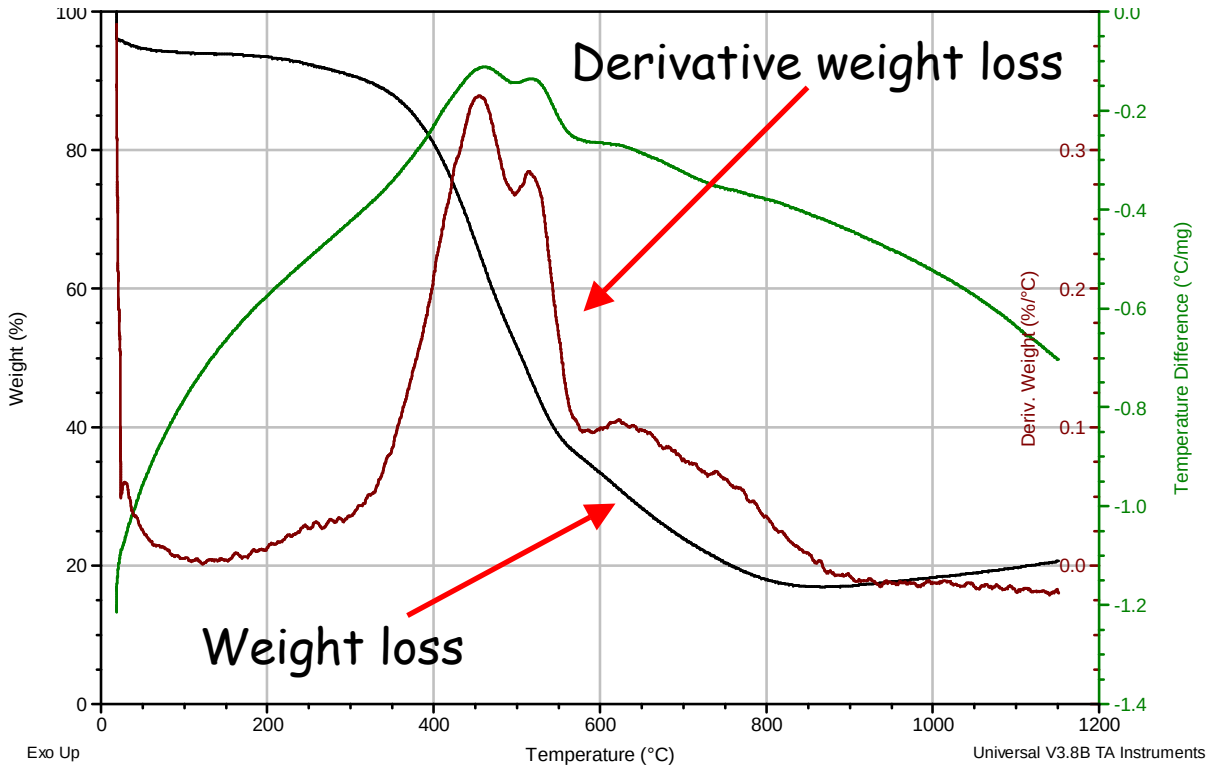
How do we obtain a reliable reference sample?

Not necessarily 100% pure, but with **known** impurities content

M. E. Itkis, et al. Nano Lett, **3**, 309 (2003)

TPO (temperature programmed oxidation)

Experiments in TGA in 100 sccm of He/O_2 mixture, 2% O_2 by volume, 5 °C/min ramp rate. Sample: Purified laser SWCNT

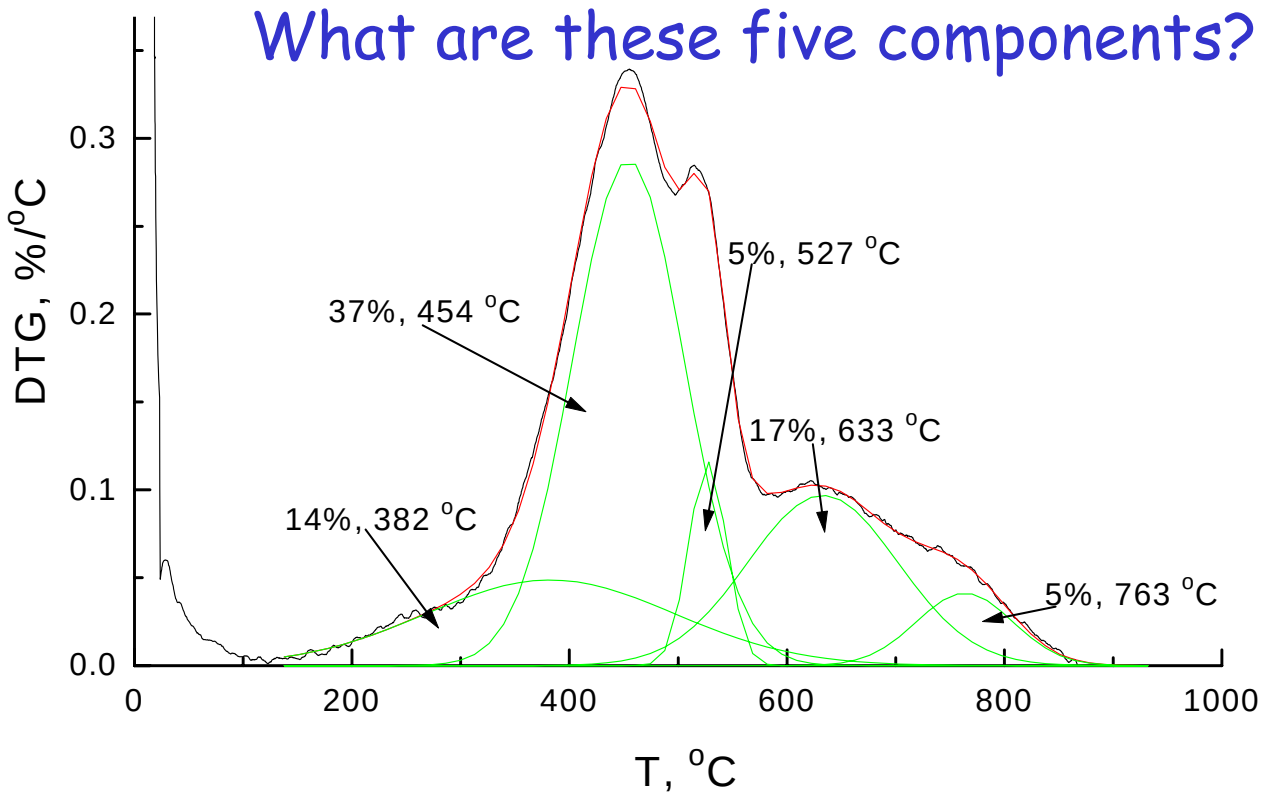


Important: unlike in air, we are seeing reliable separation of several components. This does not happen on any sample – HNO_3 treatment is important, probably extends temperature range of oxidation

Deconvolution of the weight loss profile:

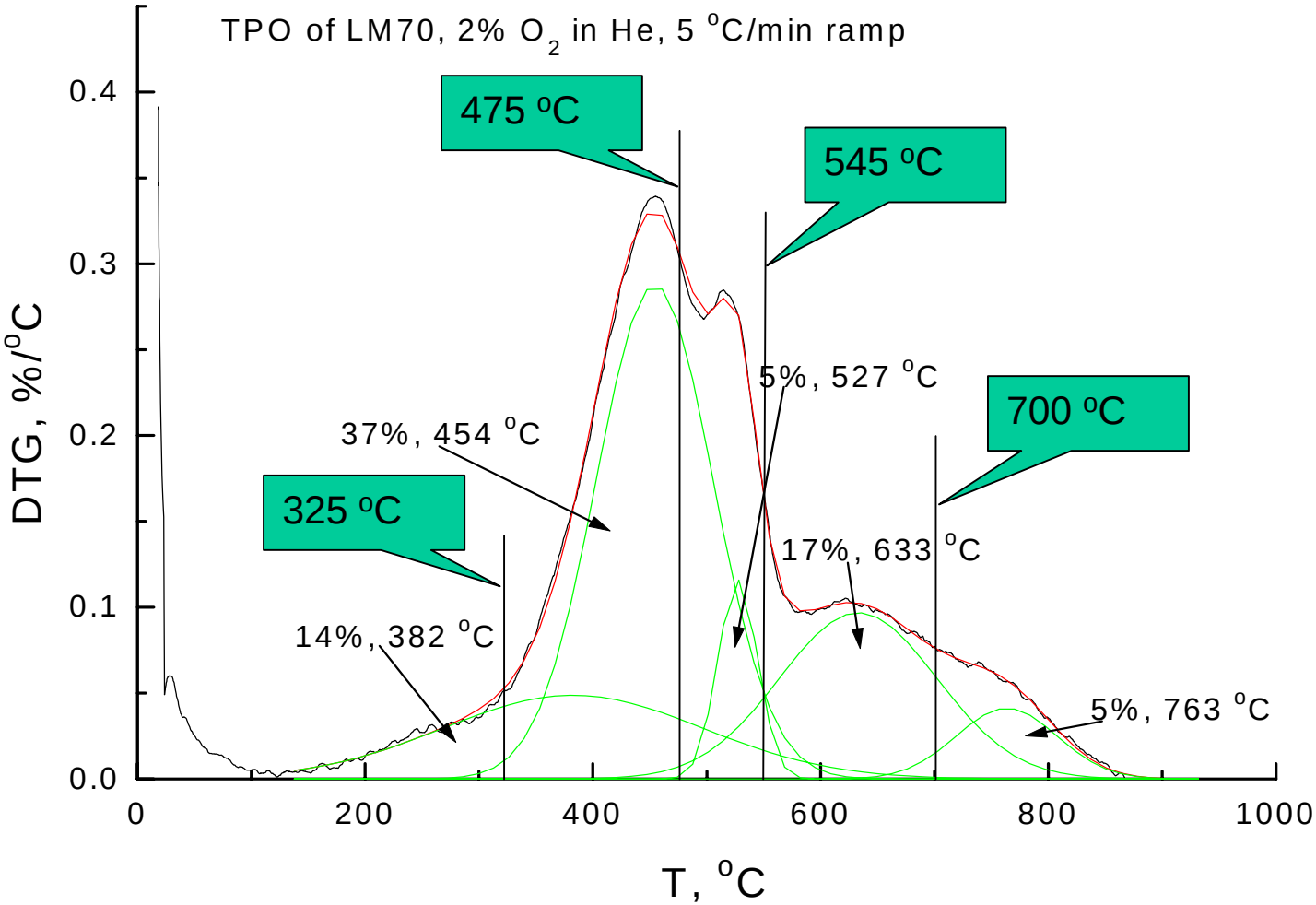
5 peaks present.
Total area under peaks is 77%. With correction for 6% initial water loss and 17% residual mass total weight loss is ~100%, as expected.
Note: the Gaussian fit of the first peak is probably unreliable.

What are these five components?

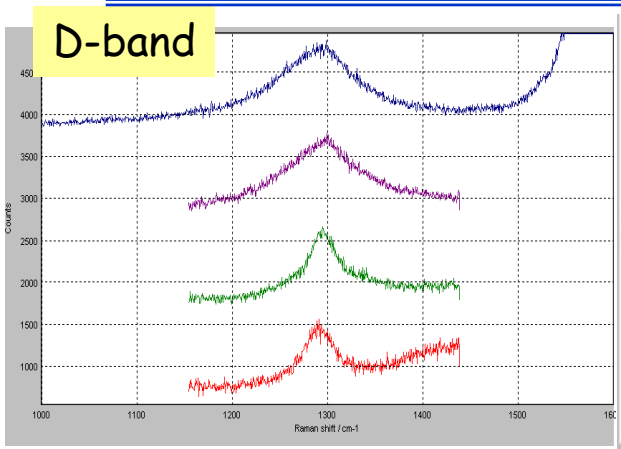


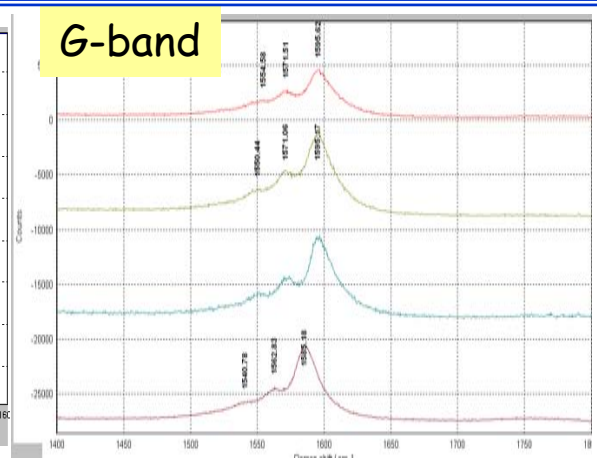
#1 – 14%
#2 – 37%
#3 – 5%
#4 – 17%
#5 – 5%

Let's stop TPO run at several temperatures and take a look at what's left.



What are these five components?





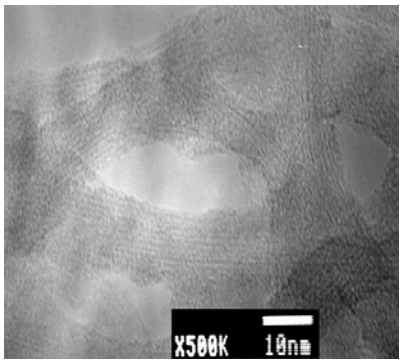
As-is: 1595 cm^{-1} G-band

325 °C: 1595 cm^{-1} G-band

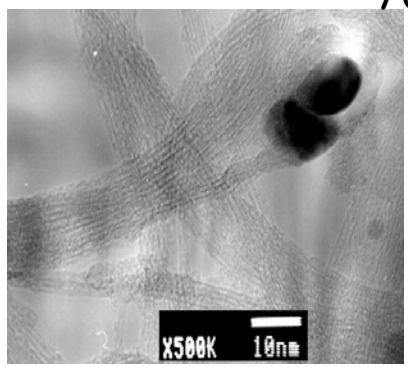
475 °C: 1595 cm^{-1} G-band

545 °C: 1585 cm^{-1} G-band

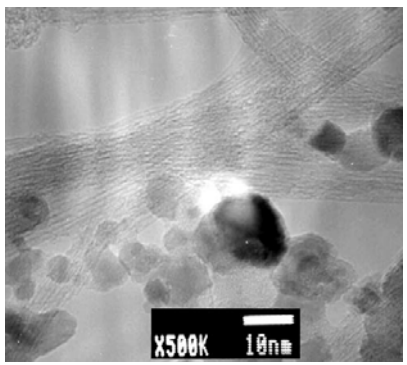
700 °C: no SWCNT signal



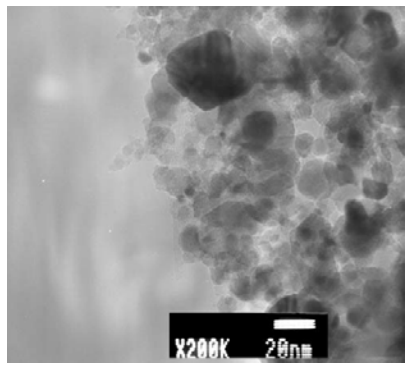
325 °C: similar to as-is



475 °C: similar to as-is but less non-tubular impurities



545 °C: even less non-tubular impurities, metal particles starting to lose graphitic coating



700 °C: no SWCNT found, metal particles and graphitic coating

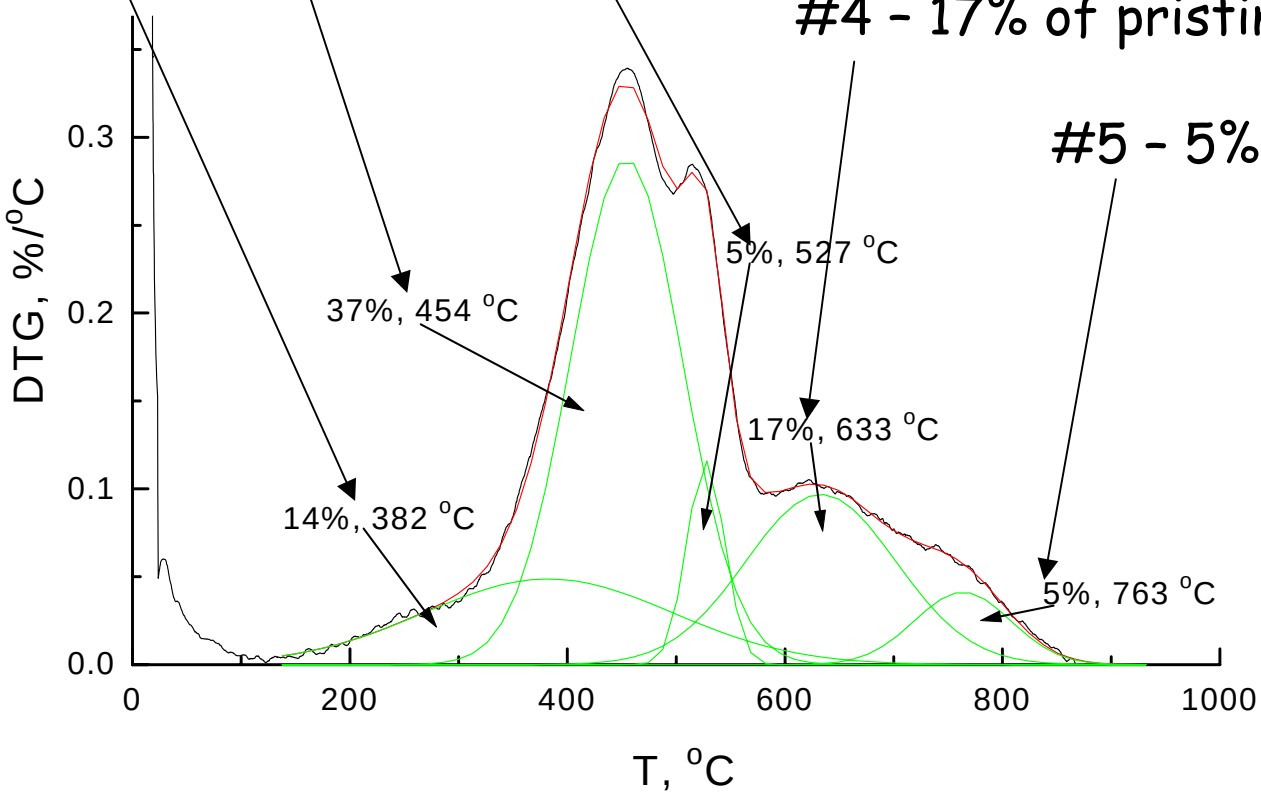
#1 – 14% of amorphous carbon (but peak area is poorly determined)

#2 – 37% of damaged NT

#3 – 5% of damaged NT

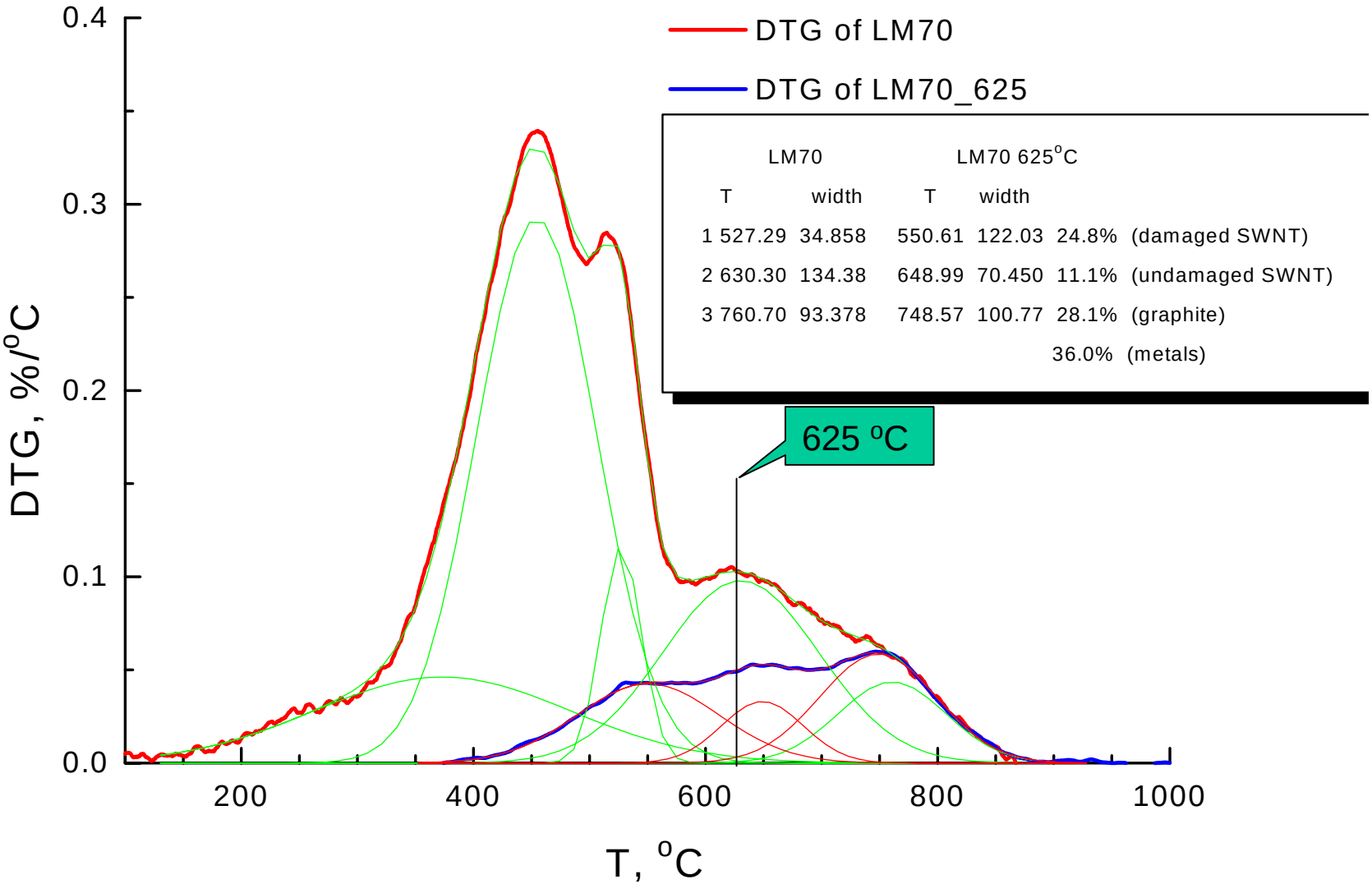
#4 – 17% of pristine NT

#5 – 5% of graphitic shells

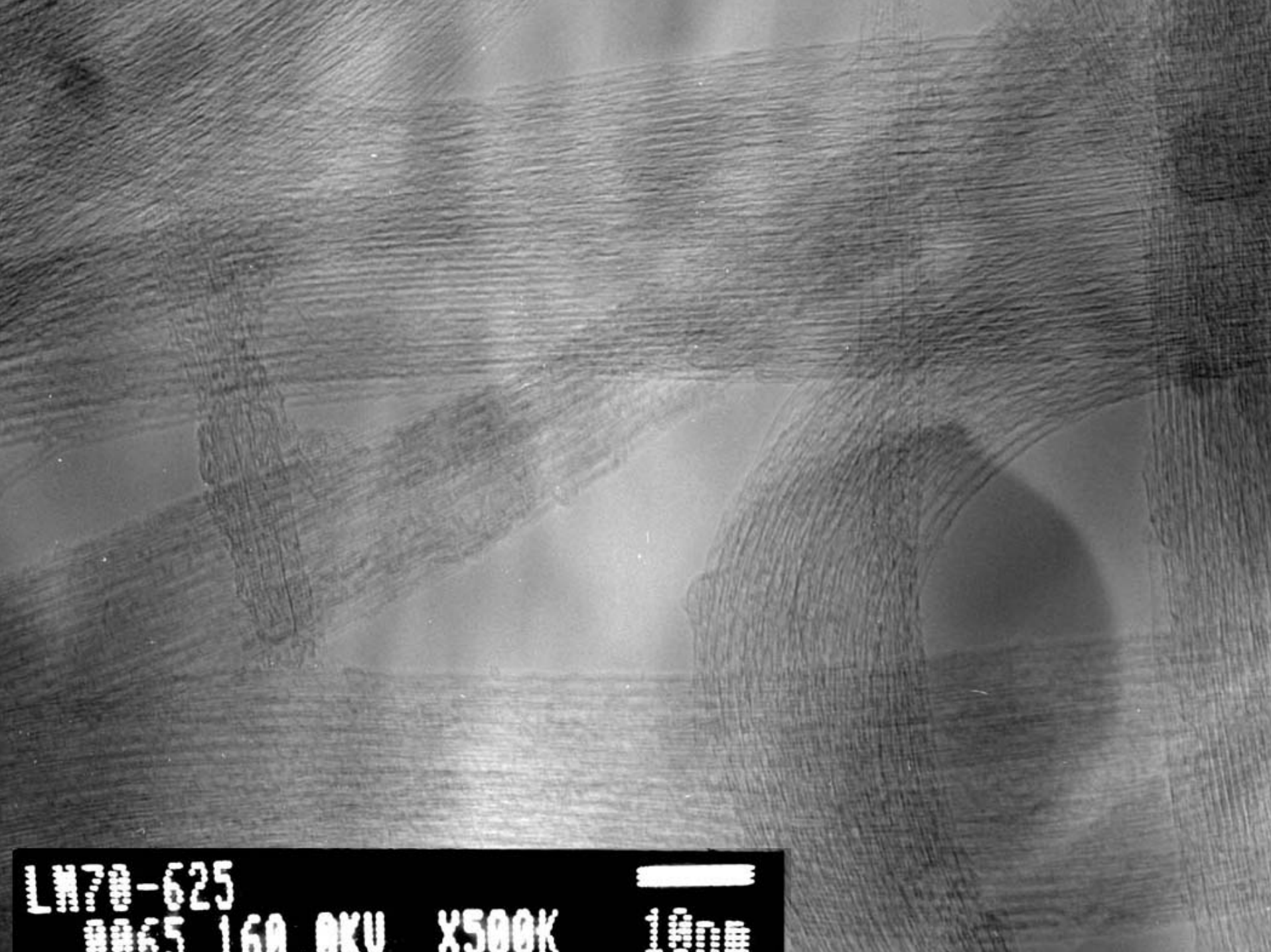


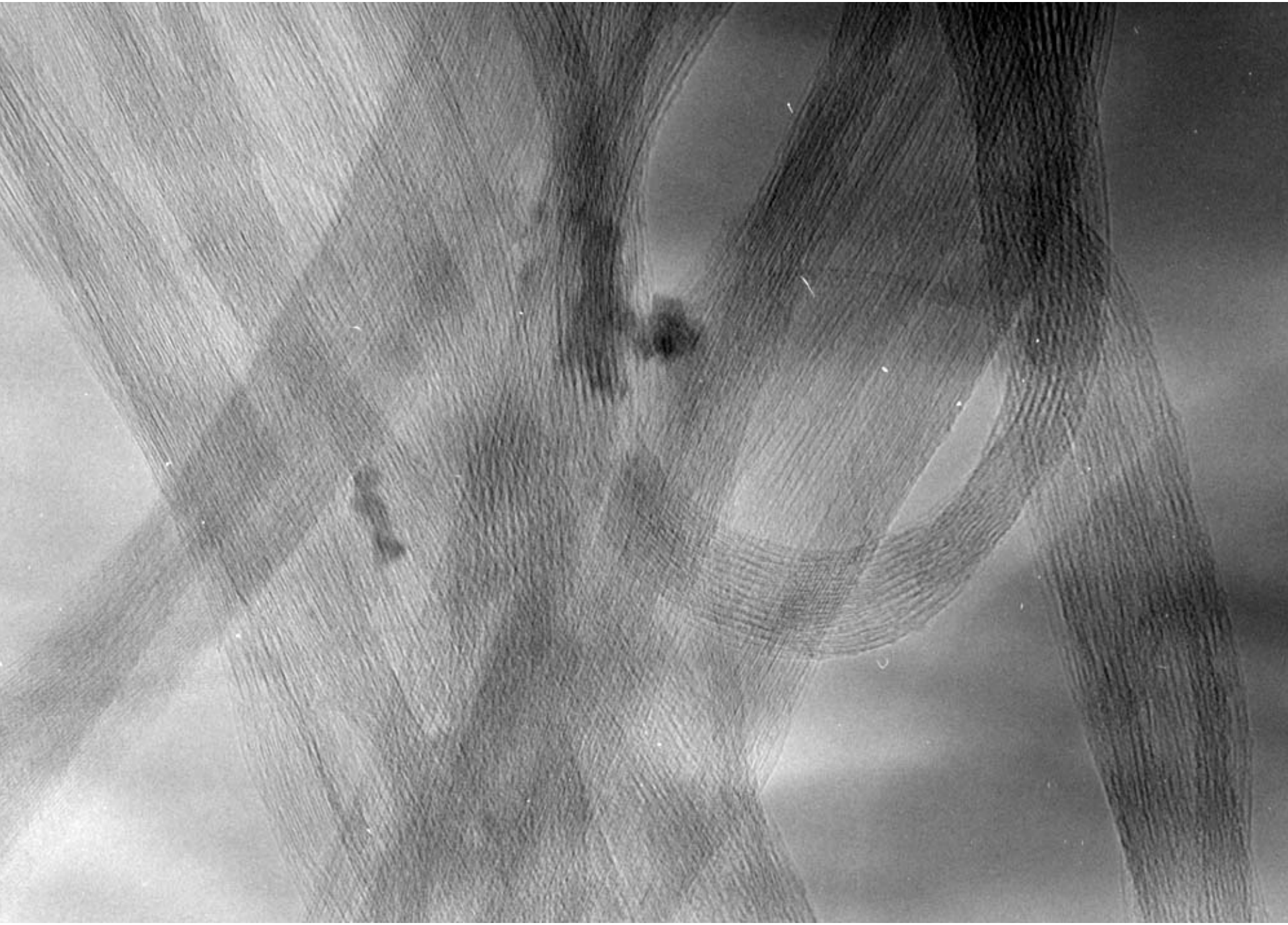
plus:
6% water
17% metal

Let's get rid of amorphous carbon altogether!



	LM70		LM70 625°C			
	T	width	T	width		
1	527.29	34.858	550.61	122.03	24.8%	(damaged SWNT)
2	630.30	134.38	648.99	70.450	11.1%	(undamaged SWNT)
3	760.70	93.378	748.57	100.77	28.1%	(graphite)
					36.0%	(metals)


LM70-625
0065 160 0KV X500K 10nm

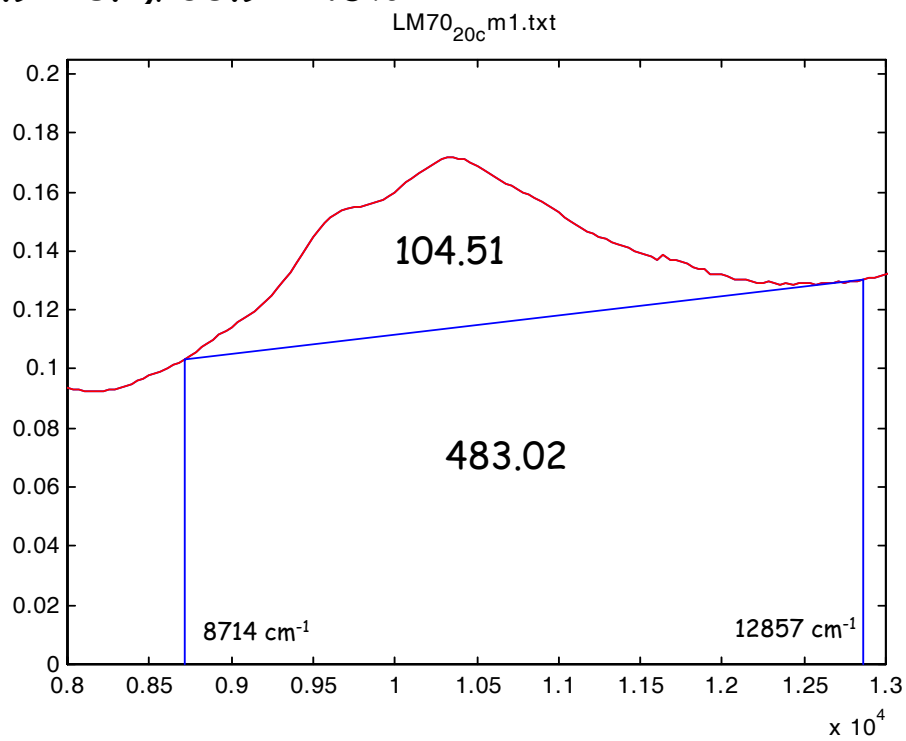


LM70-625

This sample has 35.9% NT + 28.1% non-tubular carbon impurity
(or 0.5609 : 0.4391 NT : impurity ratio, or φ=0.5609)

RP=136.28%

Assuming <u>equal extinction</u> for non-tubular carbon impurities and NT in plasmon region, relative purity of 100% NT sample is
136.28*(35.9+28.1)/35.9=**243**%



peak area =104.5098 , total area =587.5345, RP=

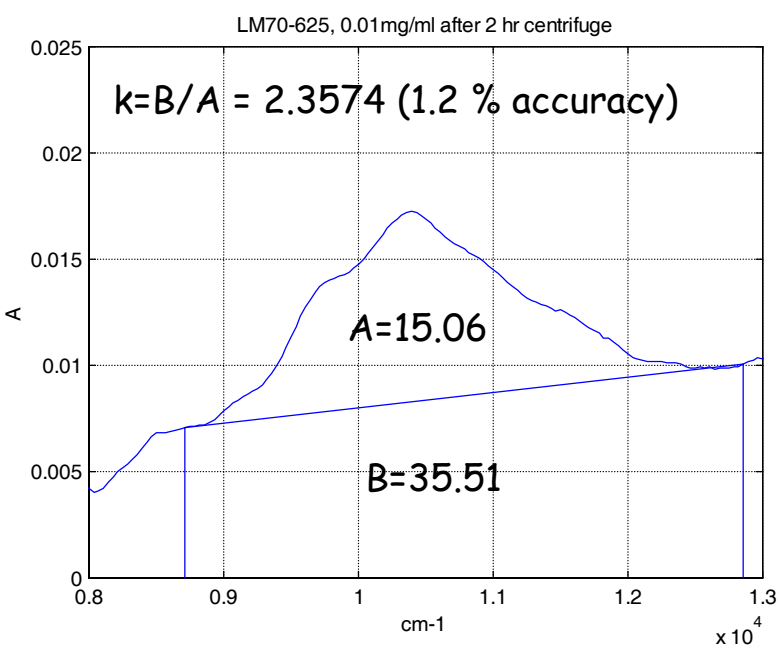
Let's get rid of graphitic particles altogether

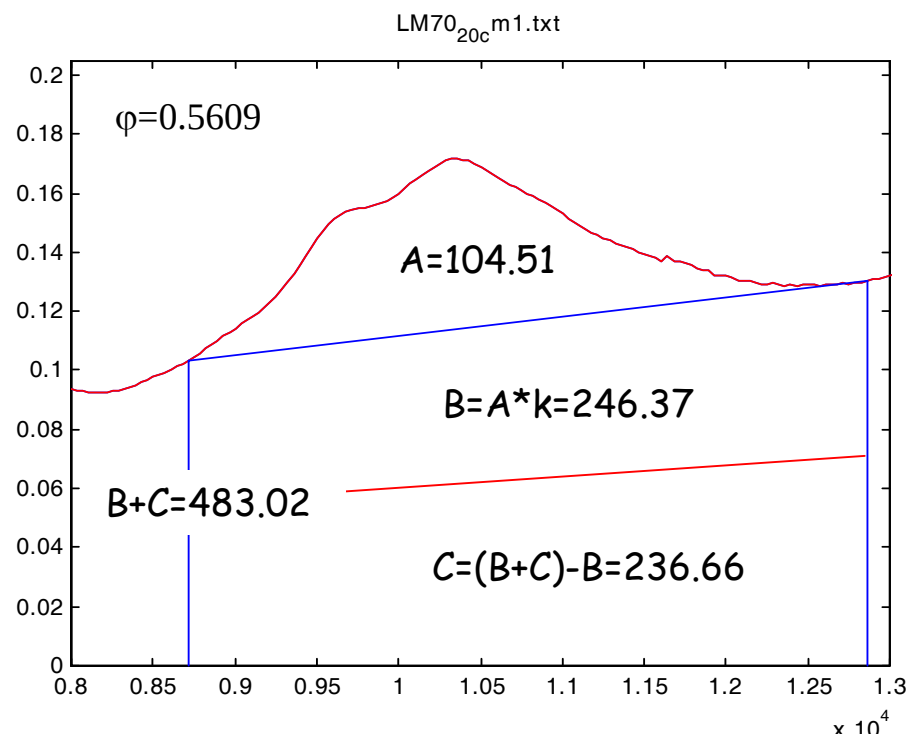
- There's no amorphous "glue" holding nanotubes and particles
- **Centrifuged for 2 hours at 20,000g.**
- Nanotube concentration decreased from 3.6 μg/ml to 0.473 μg/ml (7.6 times)
- Relative purity increased to 230.16%

Is this evidence of removal of metal/graphite particles? (to be confirmed by AA)

If we assume that this sample has NO carbonaceous impurities, then: **B/A = 2.3574**

$B = x\varphi$, $C = x(1-\varphi)\varepsilon$, $\varepsilon = \frac{\varphi}{1-\varphi}\frac{C}{B}$ = **1.2270**, meaning that NT absorb 1.2270 times stronger in the plasmon region than carbonaceous impurities.





Conclusions

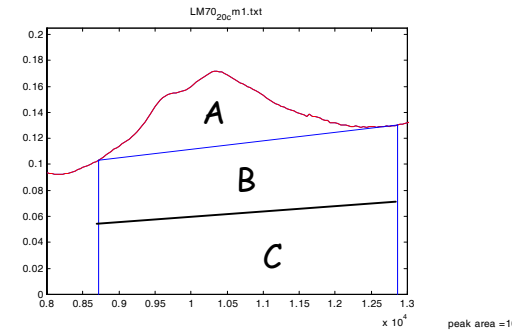
Now we have a nanotube purity standard – 100% laser SWCNT in DMF solution (~3.6 μg/ml)

k=B/A = 2.3574 (1.2 % accuracy), i.e. we can calculate NT plasmon absorption from NT Van Hove absorption.

ε = **1.2270** , i.e. absorption by NT is 1.2270 times stronger than absorption by carbonaceous impurities.

From this we can calculate absolute ratio of nanotubes to non-tubular carbon impurities in any laser NT sample, using the following strategy:

1. Measure A and (B+C)
2. Calculate B=kA
3. Calculate C=(B+C)-B
4. Calculate $\varphi = \dfrac{B}{B + C/\varepsilon}$



Combined with metal content measured by TGA, we know composition of the sample

Future work

1. Still does not work for HiPco NT – need to determine spectral window
2. Need to determine accuracy, Atomic absorption
3. Possibly need to include M_{11} hump as well – to account for possible variation in metallic/semiconducting NT ratio

Acknowledgements

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