

NANODEVICE: CNT-detect

Monitoring method for CNTs

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Markus Keller

Guido Kreck

Yvonne Holzapfel

Fraunhofer IPA

CNT-detect

CNT and Safety Issues

- CNTs are in discussion as a **potential health hazard** if inhaled.
- **Intense focus on CNTs** due to large production volume and reported health effects due to high aspect ratio.
- Industrial used are mainly **multi-walled CNTs (mwCNT)**.

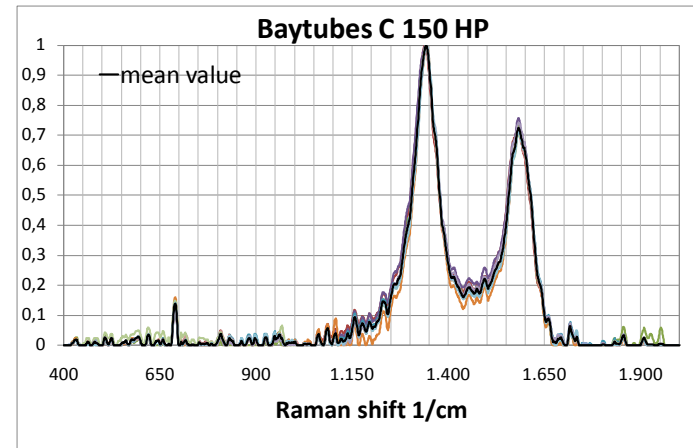
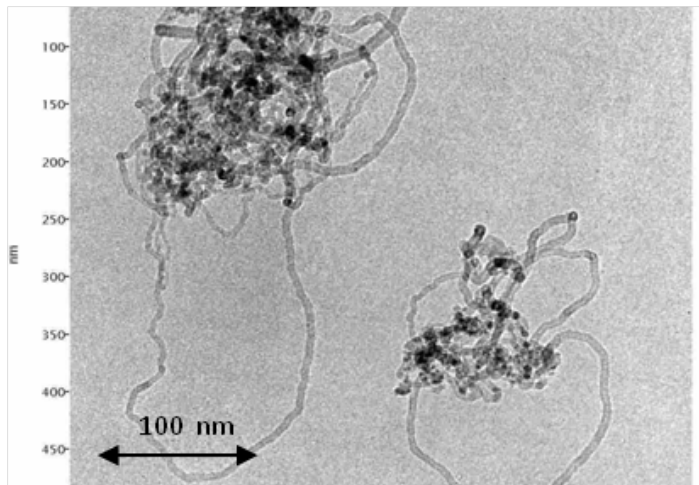


ETC Group (2007): Winners of Nano-Hazard Symbol Contest Announced at World Social Forum, Nairobi, Kenya, see http://www.etcgroup.org/upload/publication/604/02/wsffinalcontestjan24_07.pdf, accessed november, 2010.

CNT-detect

- Principle

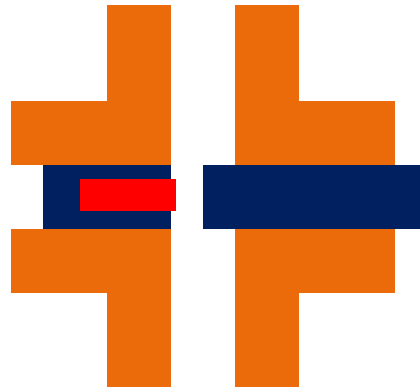
- CNTs form large-scale production processes contain mostly **cores of iron, cobalt or manganese** and are therefore ferromagnetic
- Collection of unpurified CNTs on a magnetic substrate
- Currently qualitative assessment using RAMAN inspection
- Future: Quantitative ass. based on the intensity of the RAMAN signal



CNT-detect

- Sampler

- Sampler:
 - Integrated permanent-magnetic substrate
 - RAMAN-analysis of substrate (currently offline, possible online)



CNT-detect

- Pump with sampler

- Personal sampling pump
- Battery-driven
- Flow: 6 l/h
- Duration: 8 hours (one working shift)



CNT-detect

- Storage of magnetic substrate

- Storage of substrate holder:
 - coned head for safe transport
 - elastic retainer



CNT-detect

- RAMAN analysis

- Offline: Qualitative analysis of substrate in lab
- Database comparison
- Here: Collected agglomerated CNTs are detected with 99,3 % as Baytubes HP 150.

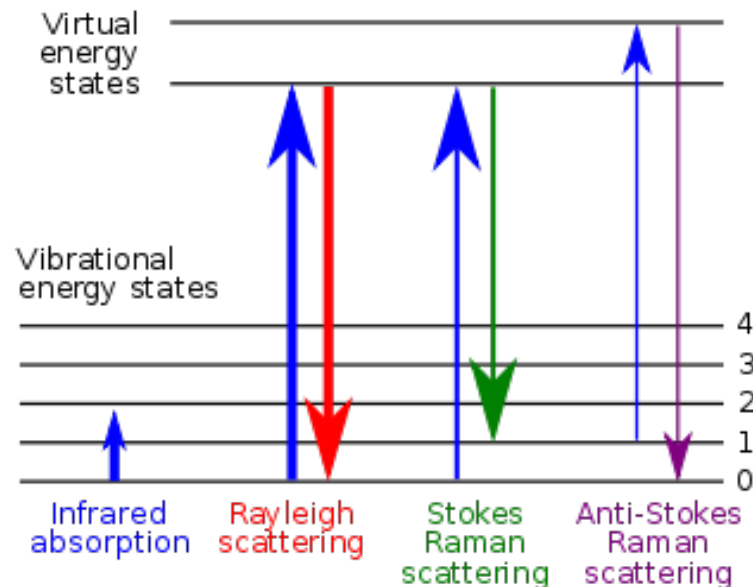
Future steps: quantification using a constant defined CNT aerosol source

Zustand Übersichtsbild	Magnet ohne Baytubes	Magnet mit Baytubes
Bild Messstelle	Magnet (Untergrund)	Baytube 1 (links) und 2 (rechts) auf Magnet
Spektrum	Magnet:	Baytube 1: Baytube 2:
Ranking	429, Background	Baytube 1: 993, Baytubes 150 HP (5) 992, Baytubes 150 HP (10) Baytube 2: 974, Baytubes 150 HP (9)

CNT-detect

- RAMAN – general

- **Raman-Effekt:** Chandrasekhara Venkata Raman; Nobelprize-winner in 1930
- Background: **Inelastic collision** between a photon and a molecule

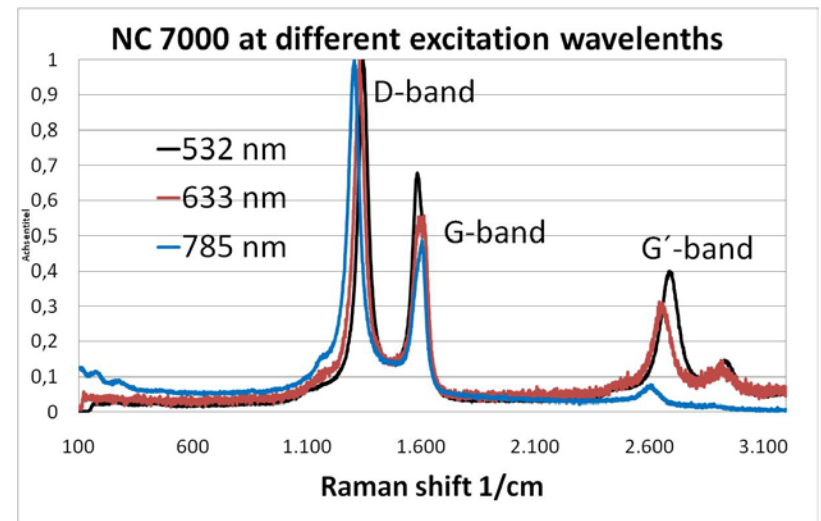


Source: Wikipedia

CNT-detect

- RAMAN – general

- **G-Band:** tangential C–C vibration between sp^2 -bonded C-atoms; characteristic for 2-D graphite layers
- **D-Band** (disorder band): typical sign for defective sp^2 -bonded graphite structures
- **G'-Band:** second-order harmonic of the dispersive disorder induced D-band
- **D/G relation:** quality of bulk sample

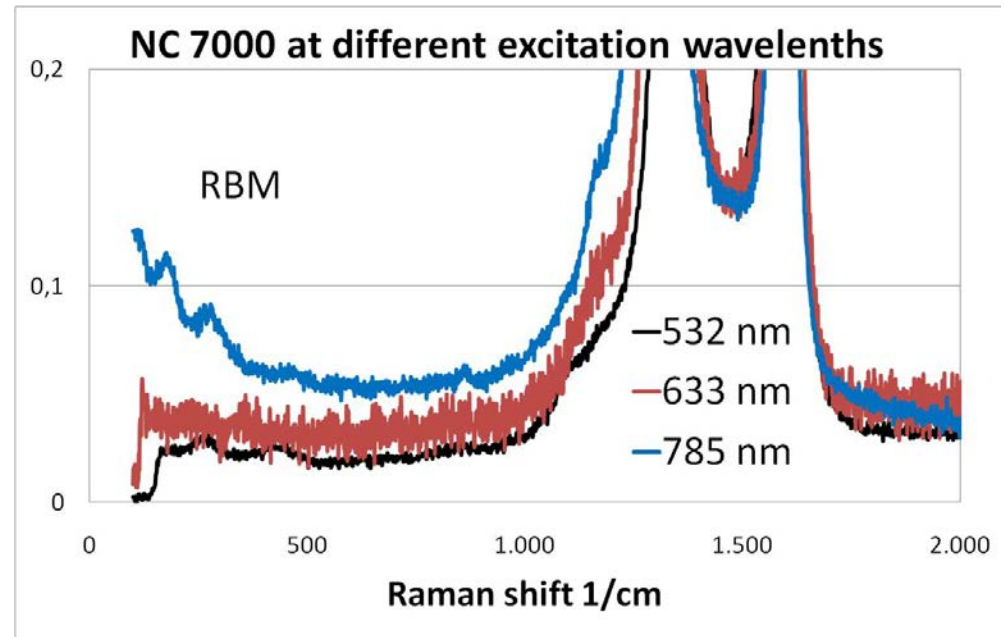


CNT-detect

- RAMAN – general

- **RBM** (radial breathing mode; Raman-shift between 100 and 250 cm^{-1}): carbon atoms move in-phase in radial direction.
- For isolated swCNT, RBM can be used to define CNT diameter :

$$\omega_{\text{RBM}} = 224/d_{\text{tube}}$$



Formula-source: Dresselhaus and Eklund, Adv. Physics 2000 **49**, 705-814

CNT-detect

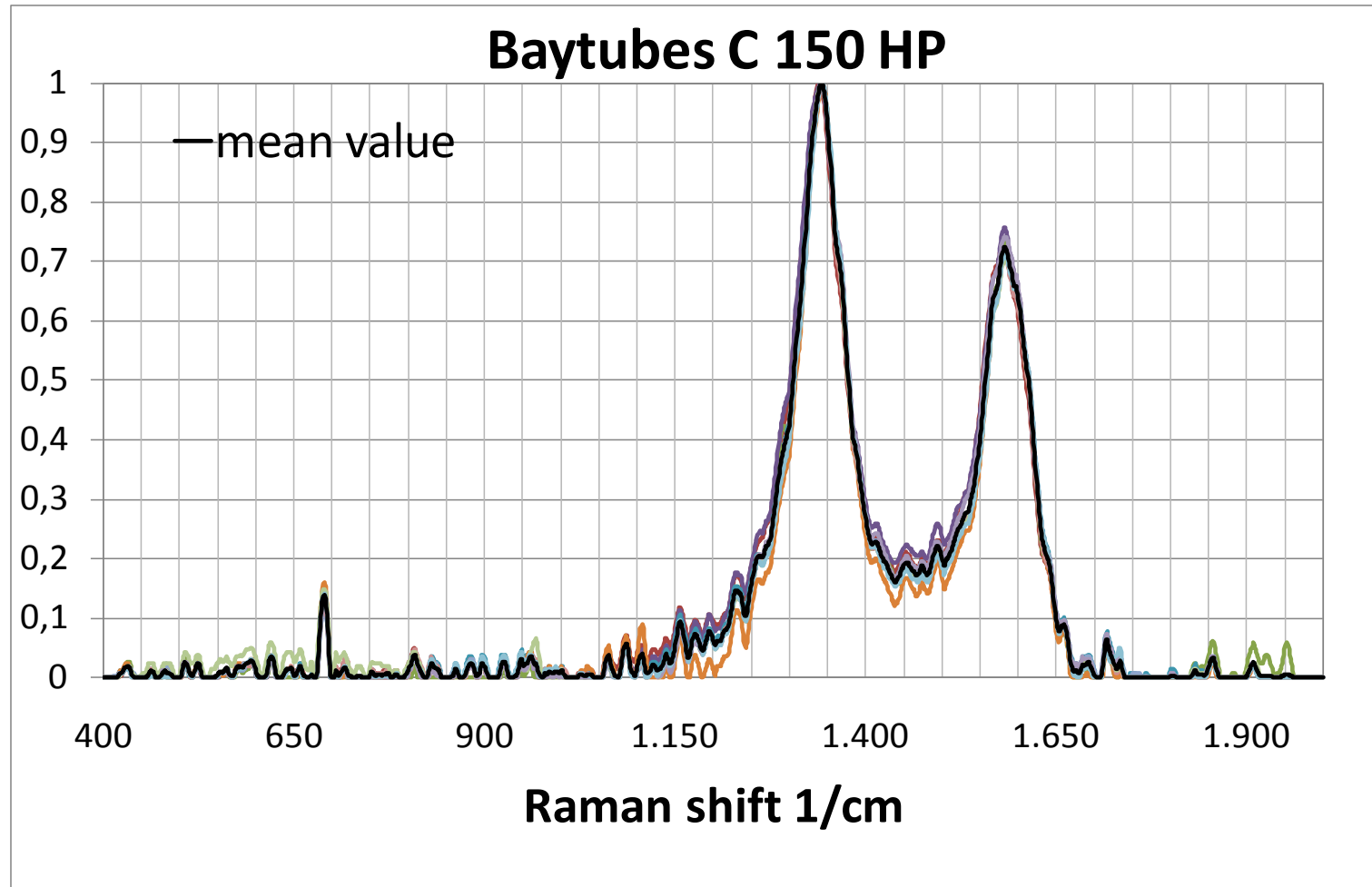
- RAMAN-analysis: database generation

- CNT-agglomerates were put directly on gold filter substrate
- Instrument: SPE CSS from Rap-ID, Berlin, Germany
- excitation wave length: 532 nm
- 10 individual measurements and resulting average
- Average spectra read into existing material database



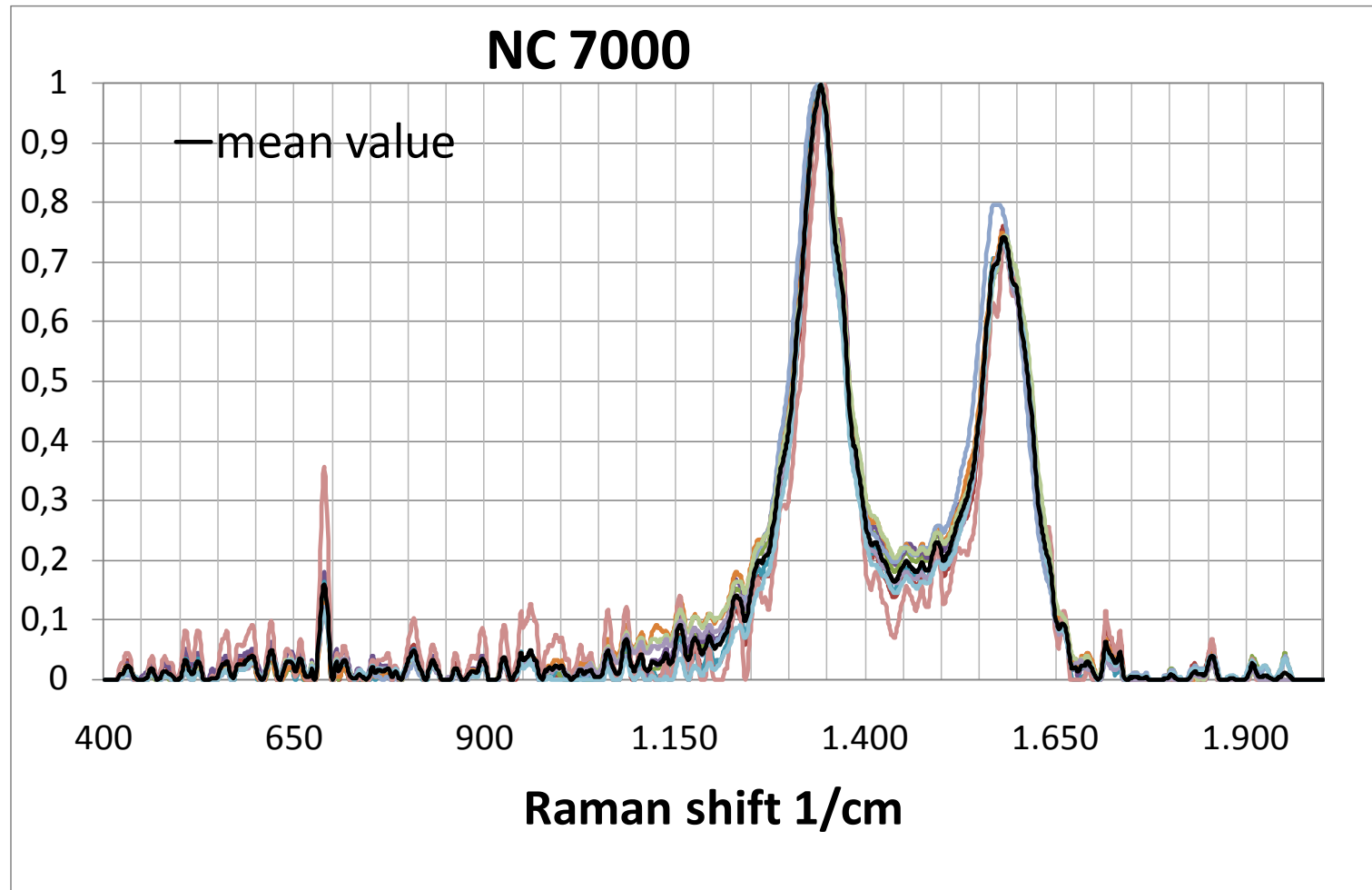
CNT-detect

- RAMAN-analysis



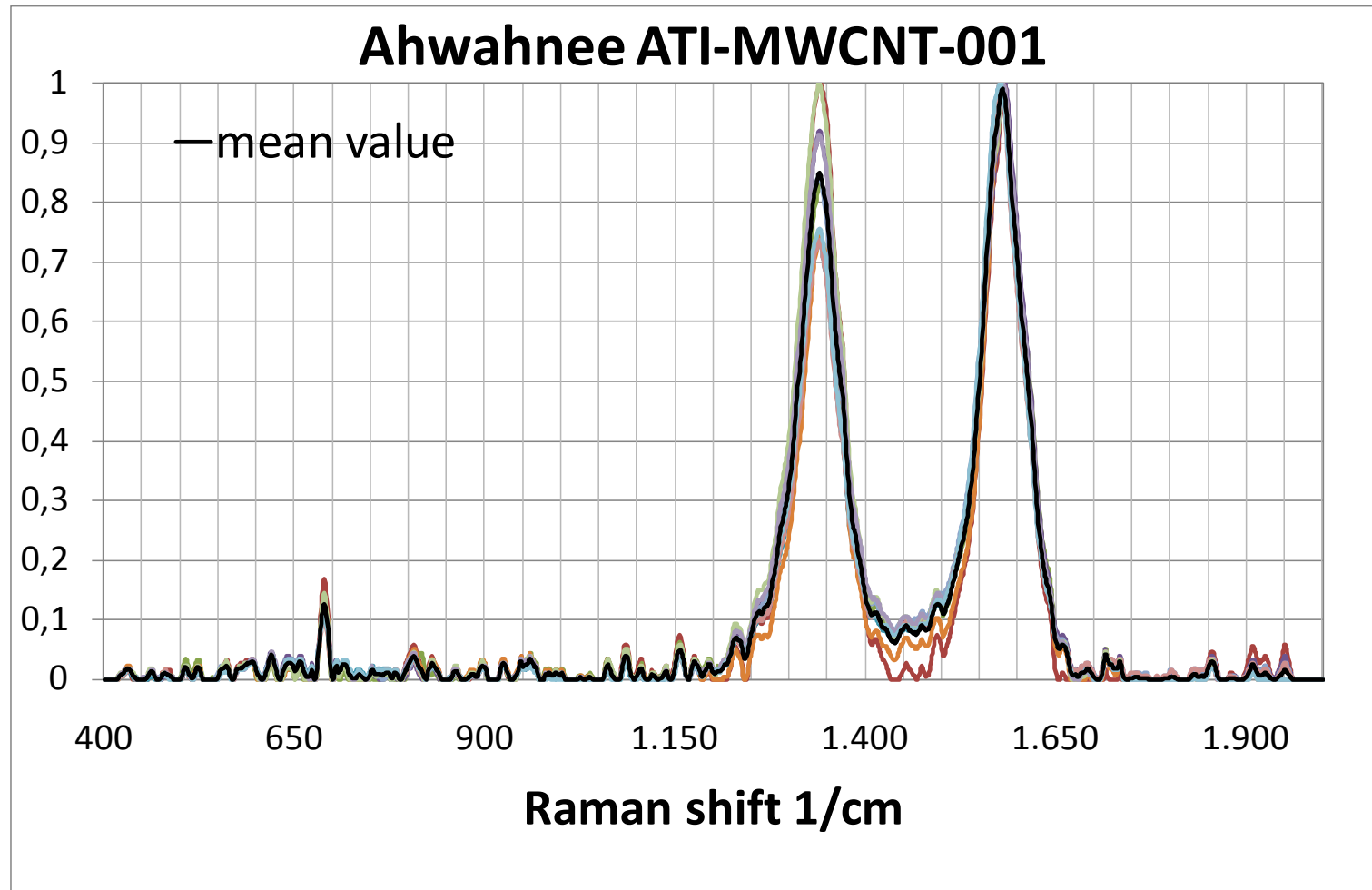
CNT-detect

- RAMAN-analysis



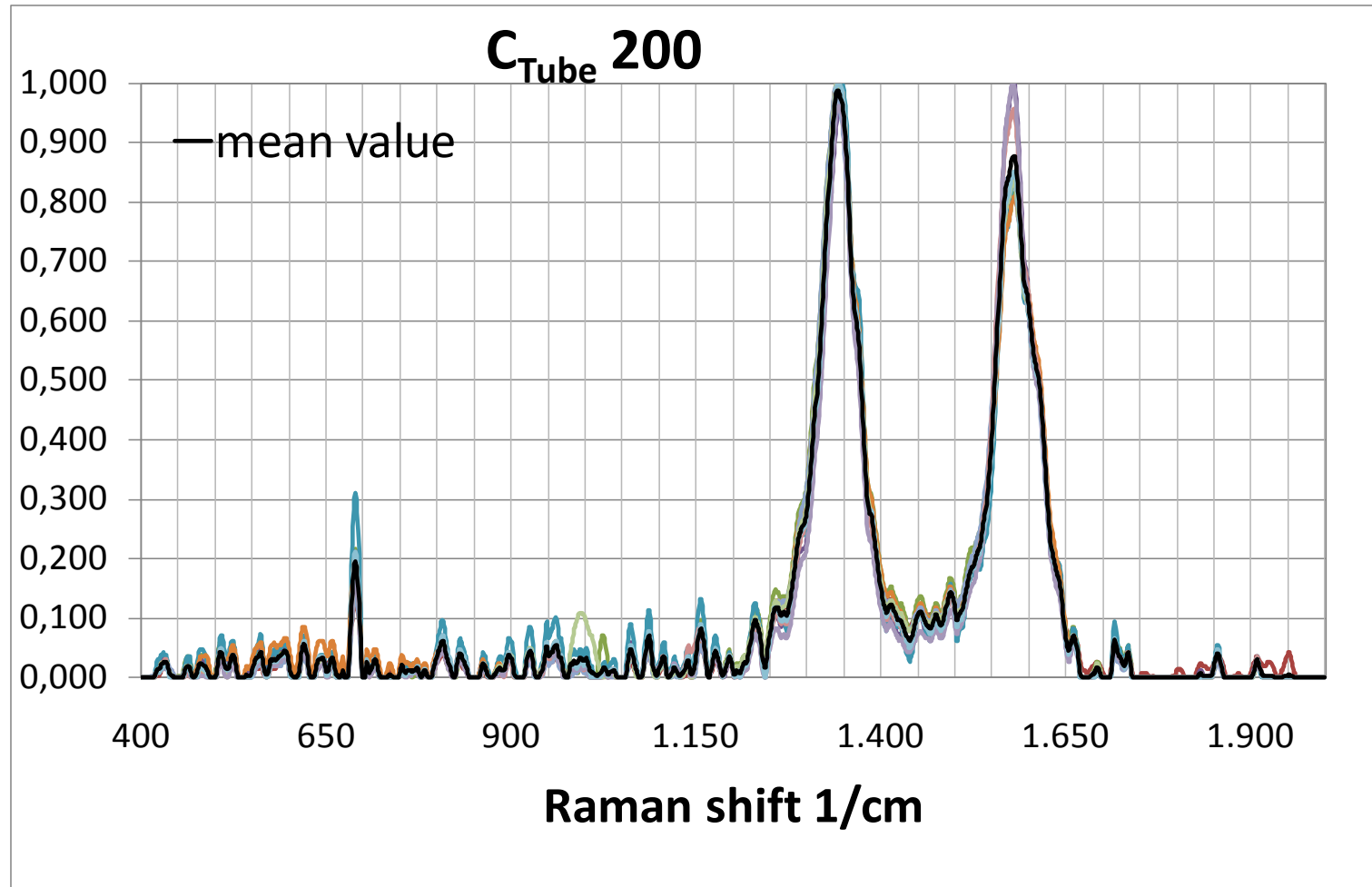
CNT-detect

- RAMAN-analysis



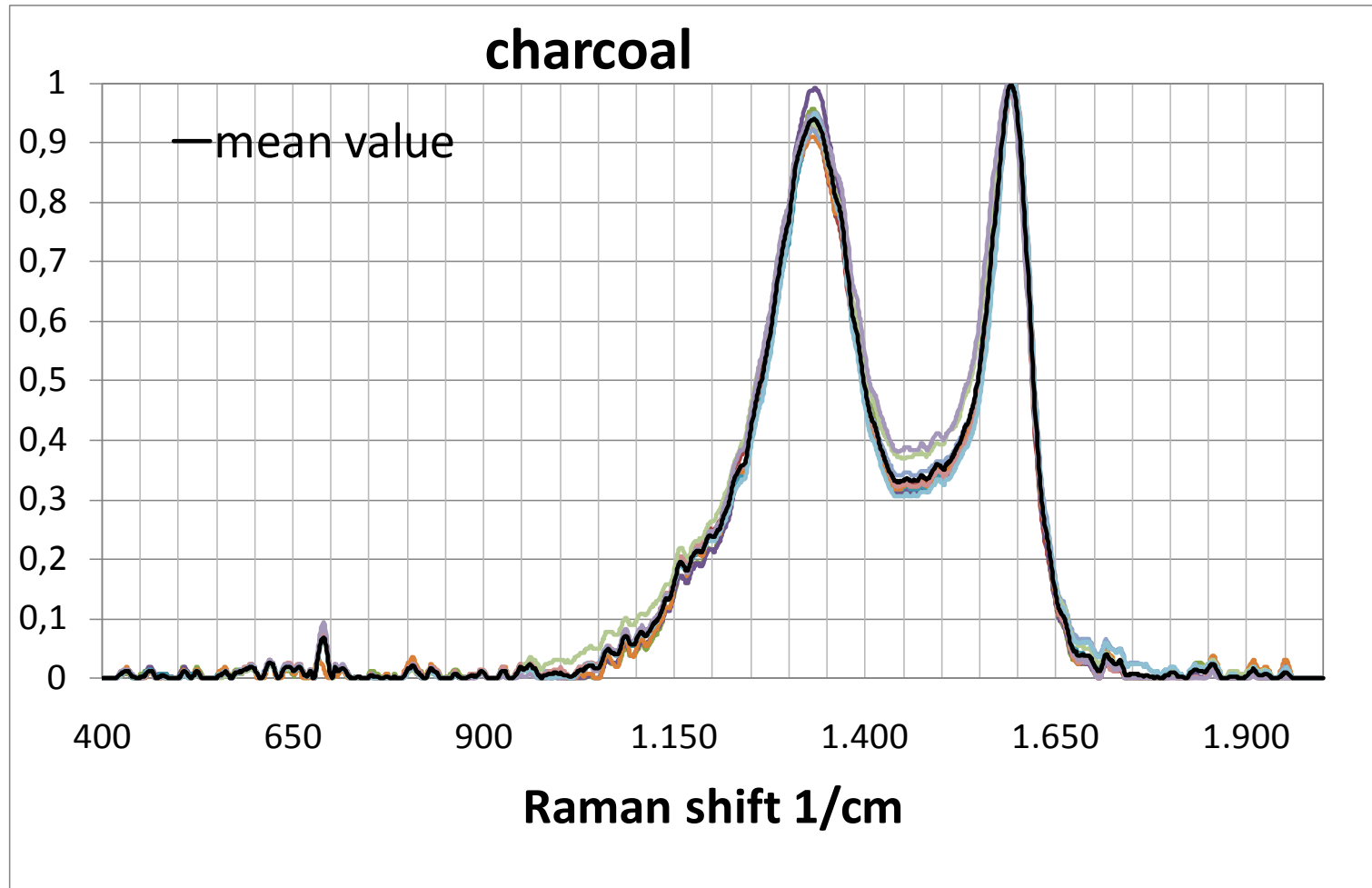
CNT-detect

- RAMAN-analysis



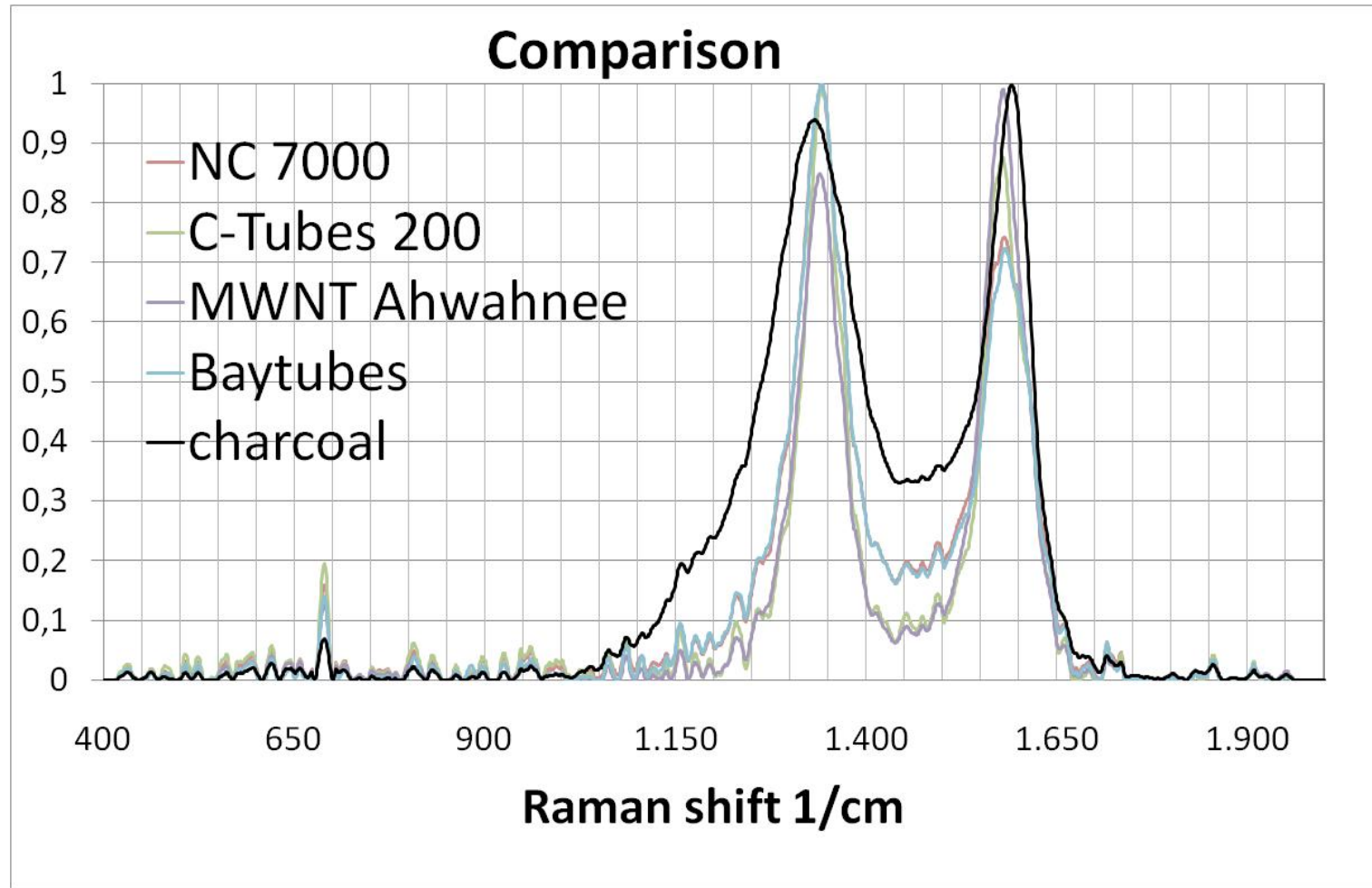
CNT-detect

- RAMAN-analysis



CNT-detect

- RAMAN-analysis



CNT-detect

- RAMAN: database comparison

- Database spectra comparison of four different CNT manufacturers and charcoal
- Correlation factor to different mwCNTs always above 98 %
- Correlation factor to non-mwCNTs always below 95 %
- **New: Even sometimes the right manufacturer was detected!**

Ahwahnee	Hit 1		Hit 2		Hit 3	
Sample ID	Result:	%	Result:	%	Result:	%
1	Ahwahnee	99.8	Ahwahnee	98.6	Ahwahnee	98.1
2	Ahwahnee	99.2	Ahwahnee	99.2	C-Tubes 200	99.1
3	Ahwahnee	99.2	Ahwahnee	99.1	C-Tubes 200	99.1
4	Ahwahnee	99.8	Ahwahnee	99.6	Ahwahnee	99.5
5	Ahwahnee	99.8	Ahwahnee	99.7	Ahwahnee	99.7
6	Ahwahnee	99.7	Ahwahnee	99.6	Ahwahnee	99.5
7	Ahwahnee	99.5	Ahwahnee	99.5	Ahwahnee	99.5
8	Ahwahnee	99.4	C-Tubes 200	98.8	C-Tubes 200	98.8
9	Ahwahnee	99.5	Ahwahnee	98.8	Ahwahnee	98.7
10	Ahwahnee	99.7	Ahwahnee	99.7	Ahwahnee	99.6

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- RAMAN: database comparison

- New: Even sometimes the right manufacturer was detected!

Ahwahnee Sample ID	NC 7000	Hit 1		Hit 2		Hit 3	
	Sample ID	Result:	%	Result:	%	Result:	%
1	1	NC 7000	99.7	Baytubes	99.6	Baytubes	99.6
2	2	Baytubes	99.1	Baytubes	99.1	Baytubes	99.0
3	3	NC 7000	99.5	Baytubes	99.4	Baytubes	99.4
4	4	Baytubes	99.6	Baytubes	99.6	Baytubes	99.6
5	5	NC 7000	99.7	Baytubes	99.6	Baytubes	99.6
6	6	Baytubes	99.8	Baytubes	99.8	NC 7000	99.8
7	7	NC 7000	99.8	Baytubes	99.7	Baytubes	99.7
8	8	Baytubes	99.5	NC 7000	99.5	Baytubes	99.4
9	9	Baytubes	99.8	Baytubes	99.8	NC 7000	99.8
10	10	Baytubes	99.2	Baytubes	98.9	C-Tubes 200	98.9

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- RAMAN: database comparison

- New: Even sometimes the right manufacturer was detected!

Ahwahnee	NC 7000	Baytubes	Hit 1		Hit 2		Hit 3	
		Sample ID	Result:	%	Result:	%	Result:	%
Sample ID	Sample ID	1	NC 7000	99.4	Baytubes	98.5	NC 7000	98.2
1	1	2	Baytubes	99.4	Baytubes	99.2	Baytubes	99.2
2	2	3	Baytubes	99.8	Baytubes	99.6	NC 7000	99.6
3	3	4	NC 7000	99.3	Baytubes	99.1	Baytubes	99.1
4	4	5	Baytubes	99.7	NC 7000	99.7	Baytubes	99.6
5	5	6	Baytubes	99.8	Baytubes	99.8	NC 7000	99.8
6	6	7	NC 7000	99.5	Baytubes	99.3	Baytubes	99.3
7	7	8	Baytubes	99.4	Baytubes	99.3	Baytubes	99.3
8	8	9	Baytubes	99.6	Baytubes	99.6	Baytubes	99.6
9	9	10	Baytubes	99.8	Baytubes	99.8	Baytubes	99.8
10	10	Baytubes	99.2	Baytubes	98.9	C-Tubes 200	98.9	
		Ahwahnee	99.7	Ahwahnee	99.7	Ahwahnee	99.9	

CNT-detect

- RAMAN: database comparison

- New: Even sometimes the right manufacturer was detected!

		Baytubes	C-Tubes 200	Hit 1		Hit 2		Hit 3	
			Sample ID	Result:	%	Result:	%	Result:	%
Ahwahnee	NC 7000	Sample ID	1	C-Tubes 200	99.3	C-Tubes 200	99.3	C-Tubes 200	99.2
	Sample ID	1	2	Ahwahnee	99.0	C-Tubes 200	99.0	C-Tubes 200	98.8
	1	2	3	C-Tubes 200	99.7	C-Tubes 200	99.7	C-Tubes 200	99.7
	2	3	4	C-Tubes 200	99.8	C-Tubes 200	99.7	C-Tubes 200	99.7
	3	4	5	Ahwahnee	99.5	C-Tubes 200	99.3	C-Tubes 200	99.2
	4	5	6	C-Tubes 200	99.9	C-Tubes 200	99.8	Ahwahnee	99.6
	5	6	7	C-Tubes 200	99.6	C-Tubes 200	99.5	C-Tubes 200	99.4
	6	7	8	C-Tubes 200	99.7	C-Tubes 200	99.7	C-Tubes 200	99.6
	7	8	9	C-Tubes 200	99.7	C-Tubes 200	99.5	C-Tubes 200	99.5
	8	9	10	C-Tubes 200	99.6	C-Tubes 200	99.6	C-Tubes 200	99.6
9	10	10	Baytubes	99.8	Baytubes	99.8	Baytubes	99.8	
10		Baytubes	99.2	Baytubes	98.9	C-Tubes 200	98.9		
		Ahwahnee	99.7	Ahwahnee	99.7	Ahwahnee	99.9		

CNT-detect

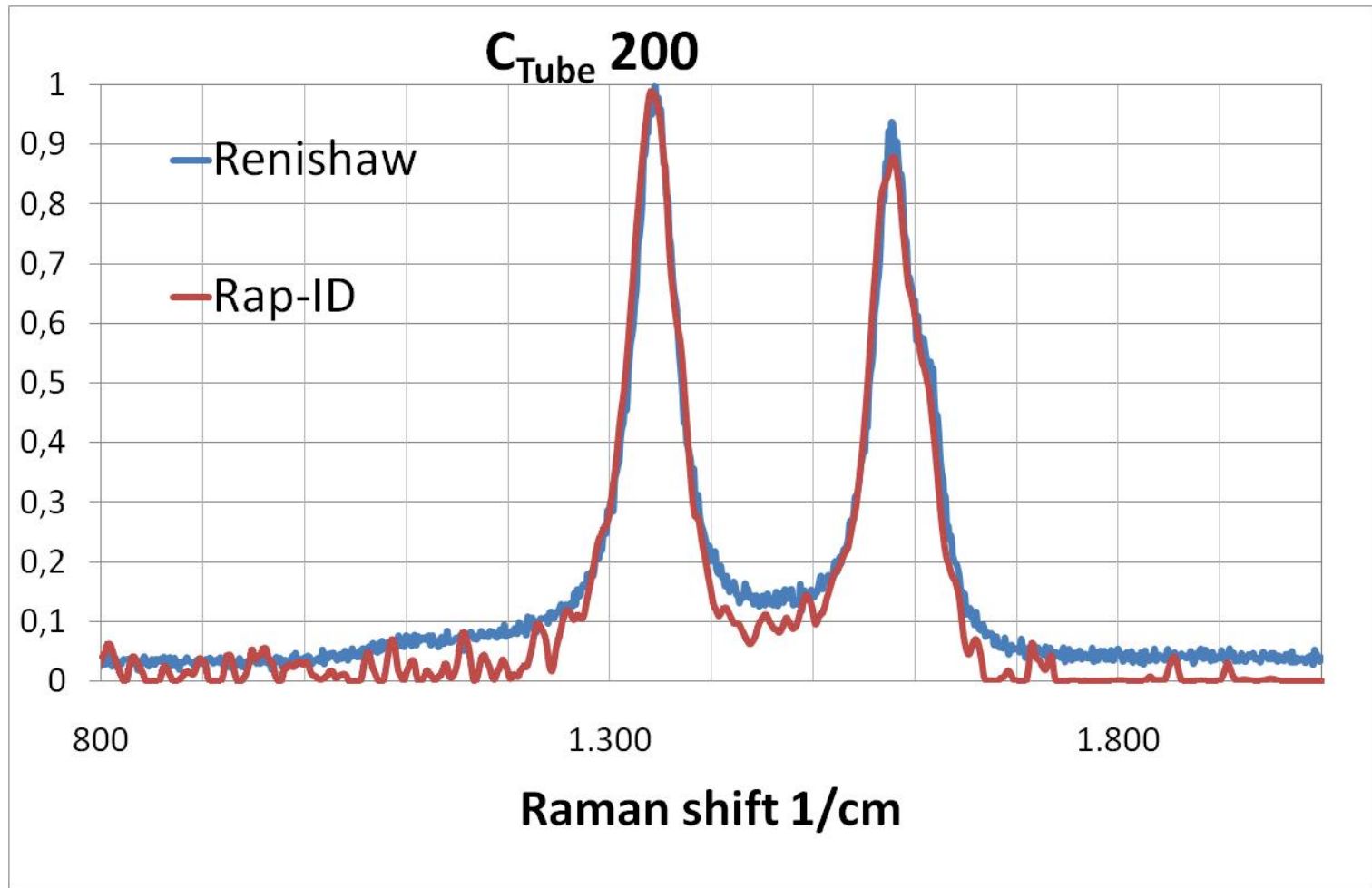
- Intercomparison of instruments

- Instruments:
 - SPE CSS from Rap-ID GmbH, Berlin, Germany
 - inVia Raman microscope, Renishaw GmbH, Pliezhausen
- excitation wave length: 532 nm
- **Result: Peak shape and peak wave number equal from both instruments**
- **CNT spectra database can be used for different instruments**



CNT-detect

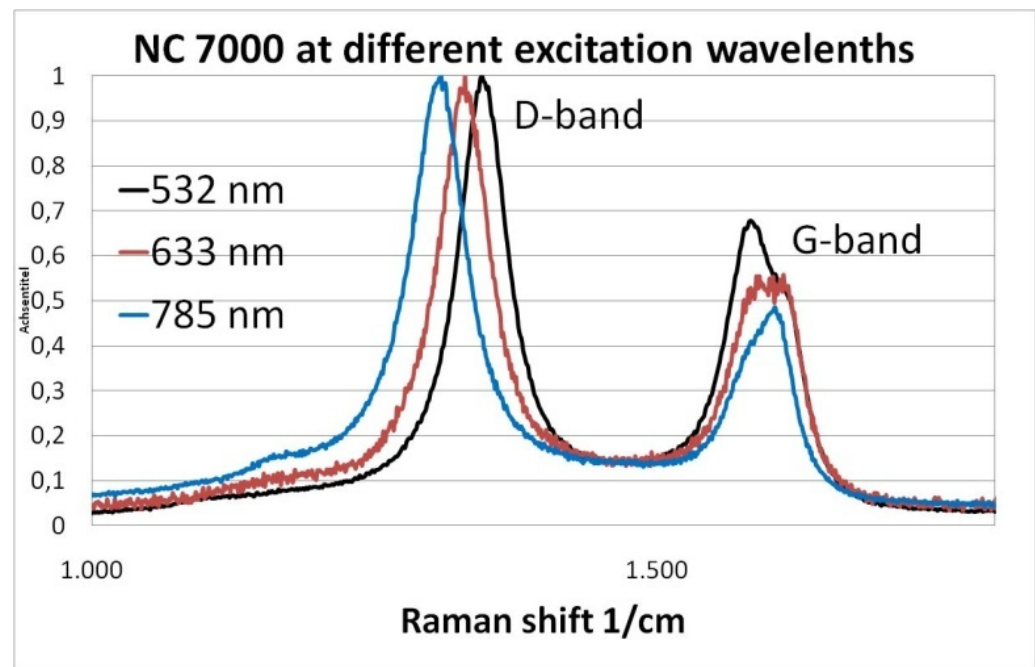
- Intercomparison of instruments



CNT-detect

- Intercomparison of different wavelengths

- Instrument: inVia Raman microscope, Renishaw GmbH, Pliezhausen
- Excitation wave lengths: 532 nm, 633 nm and 785 nm
- **Result: Peak shape and peak wave number depends from exitation wavelength**



CNT-detect

- Outlook

- Real scenario measurements (currently ongoing)
- Calibration with different CNT concentrations in aerosols: a constant defined CNT source is needed for this task!
- Limit of detection?
- Usage of miniaturized portable RAMAN spectrometer

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Questions? Contact:

*Markus Keller – Fraunhofer IPA – Dept. Ultraclean technology and
Micromanufacturing – Nobelstr. 12 – D-70569 Stuttgart – Germany –
phone +49-711-9071560 – mail: markus.keller@ipa.fraunhofer.de*

