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Elemental carbon (EC) measurement as a method to estimate workplace exposure to airborne nano-carbon materials

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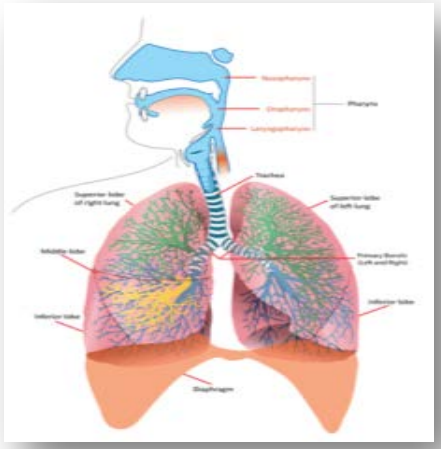
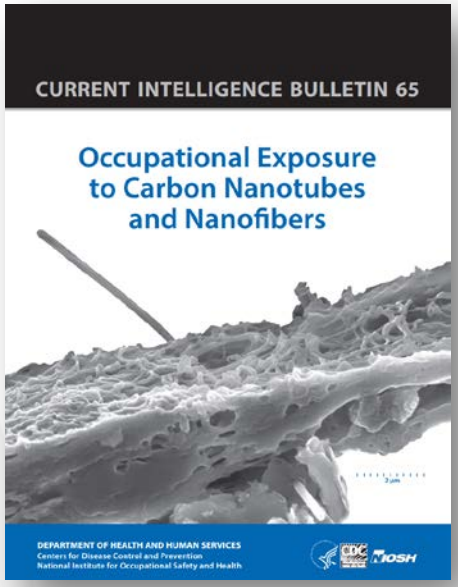
Introduction

- Carbon nanotubes (CNT) and carbon nanofibres (CNF) are considered a potential respiratory hazard – morphology driven hazard
- Currently, no ***statutory*** occupational exposure limits for CNT or CNF
- NIOSH Current Intelligence Bulletin (2013) currently recommends exposure to CNT & CNF below a **Recommended Exposure Limit (REL)**
  - 1 µg/m^3 of Elemental Carbon as a respirable mass over an 8-hr TWA – when predominant source of EC is CNT & CNF
  - Other metrics relevant- electron microscopy analysis for morphology and elemental characterisation





Case study- objectives

UltraWire

Ultra Conductive Copper-Carbon Nanotube Wire

- Exposure assessment to characterise releases and potential exposures to CNT in the workplace environment
- Consider different types of activities
  - Synthesis of CNT and material recovery
  - Handling of CNT in the production of nanocomposites
  - Transformation of composite materials into final products
  - Recycling of composite material
- Based on evidence gathered during the assessment provide recommendations for safe working to minimise exposure

Case study- exposure assessment to date

Activities	Number of companies	Type of material	CNT quantities handled	Composite quantities handled
CNT Manufacturer	1	SWCNT/ MWCNT	< 1 kg	-
Production of nanocomposites	3	SWCNT/ MWCNT CNT yarns	<1 g (3) <10 g (1)	<1 kg (3) <10 kg (1)

Further data to be gathered:

- Transformation of composite materials into final products
- Recycling of composite materials

Methodology- Elemental Carbon (EC) sampling

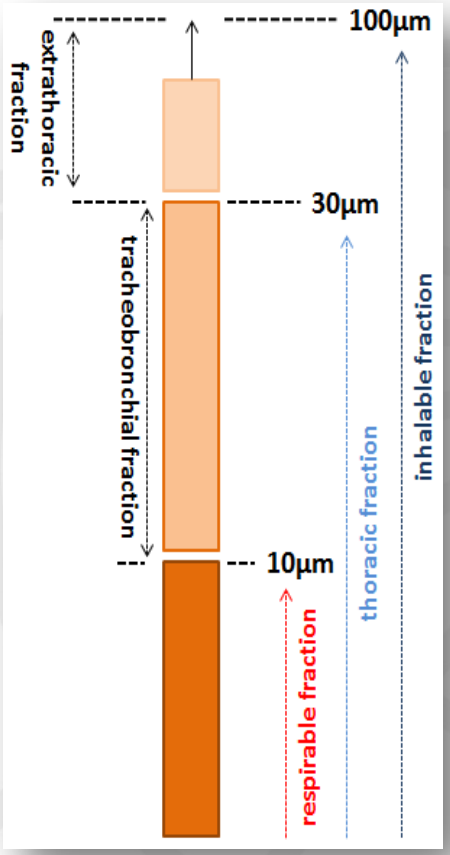
- EC analysis using NIOSH analytical method 5040- EC used as a proxy for CNT
  - Air samples collected onto 25 mm cassettes containing a heat-treated quartz filters
  - Thermal-optical analysis- FID detector
- Detection limit of the method is 1 µg/m^3 = the REL for EC as a respirable mass over an 8-hr TWA
- Sources that can influence the determination of EC in the workplace include diesel engines, gas burners, carbon black

Methodology- particle sampling

- Sampling undertaken in the personal breathing zone (PBZ), in the near-field (area around the activity) and in the far-field
- Background characterisation undertaken- establish background sources of EC
- Multiple exposure metric approach was adopted - air samples also collected for Scanning Electron Microscopy / Energy Dispersive X- ray Spectroscopy analysis (SEM/EDXS)

Methodology- particle sampling

- Air samples collected for SEM analysis- including size selective sampling (respirable fraction)



Respirable Cyclone

d_{50}<4µm AED

2.2 l/min

Analysis by SEM / EDXS

Nano-ID

250nm - 35µm AED

Size-fractionated sampling on 7-stages.
20 l/min

Analysis by SEM / EDXS

Cowl Head

Non-size selective particle sampling.
2.2 l/min

Analysis by SEM / EDXS

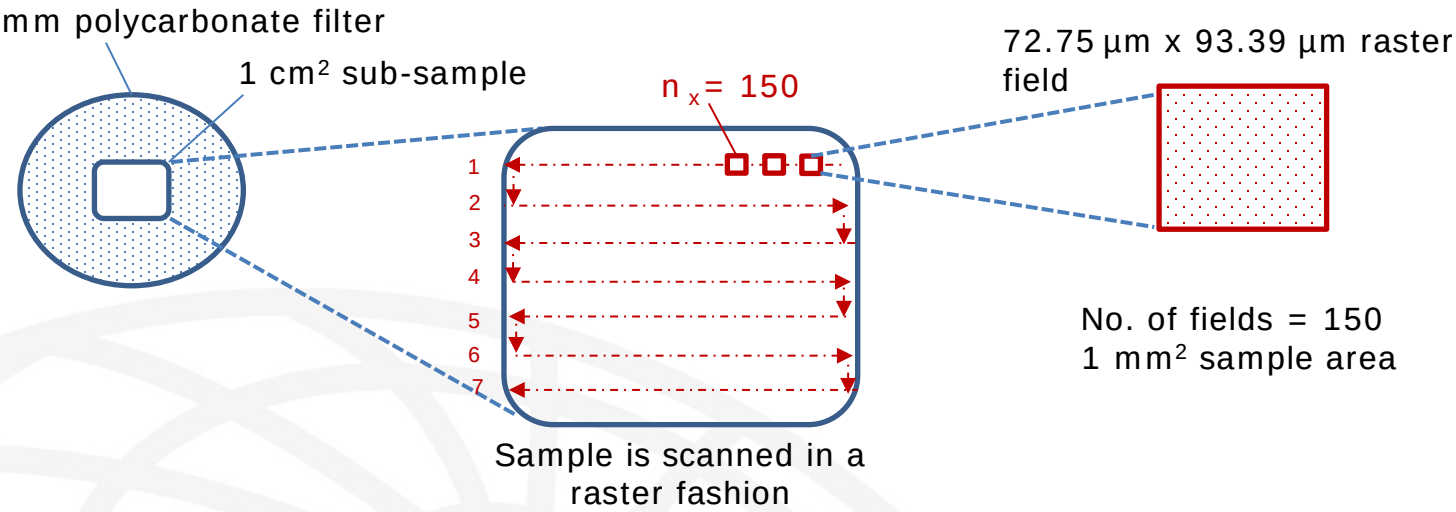
25mm Cassette

Quartz Filter

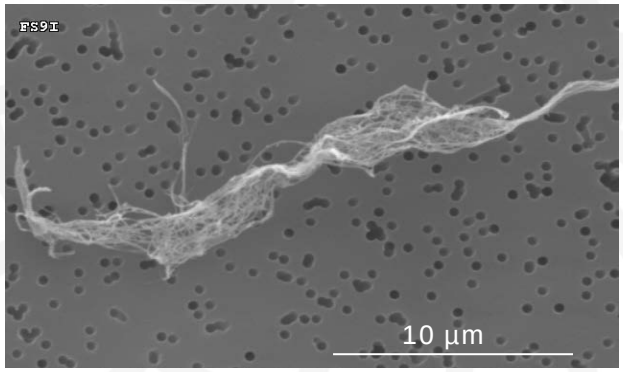
Non-size selective particle sampling.
2.2 l/min

Samples analysed for Elemental Carbon as a proxy for CNT / CNF / Graphene

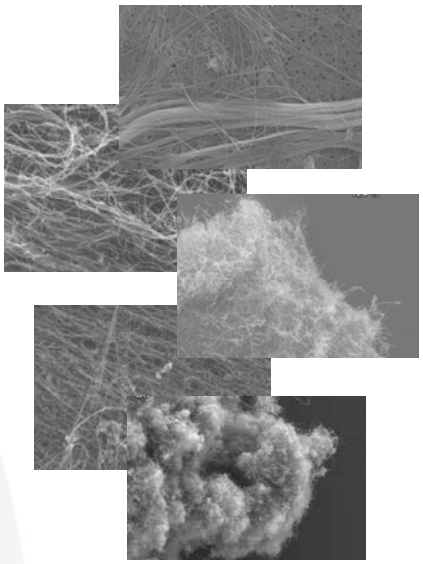
Methodology- fibre counting



Scanning Electron Microscope Hitachi: S-2600N



= 1 CNT structure



ISO 14966:2002: "Ambient Air – Determination of numerical concentration of inorganic fibrous particles – Scanning electron microscopy method".

Samples – EC & SEM analysis

Activities	Number of EC samples			Total
	Near-field	PBZ Inhalable	Far-field	
CNT Manufacturing, recovery and testing	2	1	1	4
Production of nanocomposites	3	3	-	6

Activities	Number of samples for SEM			Total
	Near-field cowl	PBZ Repirable	Nano-ID high volume sampling	
CNT Manufacturing, recovery and testing	3	1	1	5
Production of nanocomposites	3	3	3	9

Results- EC analysis

Activities	Number of samples			8-hr TWA (µm/m³)	
	Total	< method detection limit of 1 µg	> method detection limit of 1 µg	Min	Max
CNT Manufacturing, recovery and testing	4	4	0	-	-
Production of nanocomposites	6	4	2	1.89	2.84

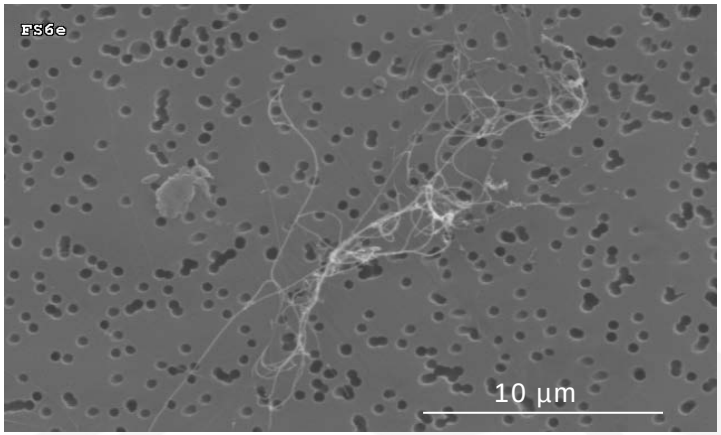
- above REL 1 µg/m³ of Elemental Carbon (8-hr TWA)
- Near-field during composite manufacture and overnight after powder handling (looking at persistence)

Results- SEM analysis

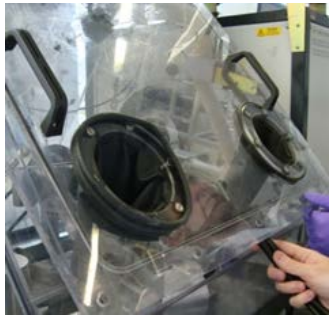
Activities	Number of samples		SEM analysis	
	Total	With CNT structures	f/cm³	8-hr TWA (f/cm³)
CNT Manufacturing, recovery and testing	5	3	0.002-0.04	0.004 – 0.01
Production of nanocomposites	9	0	-	-

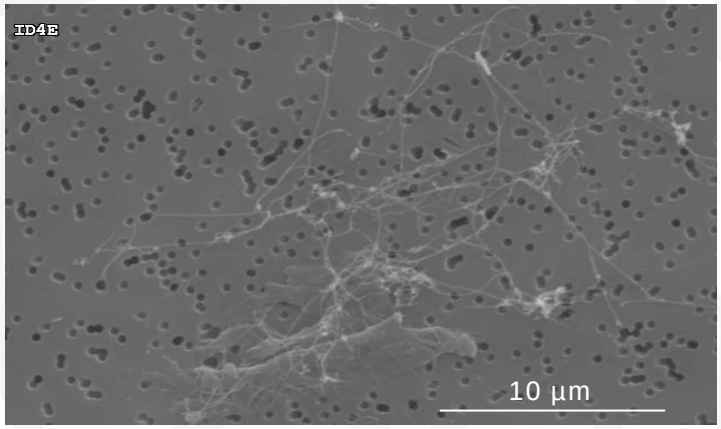
- No established CNT counting methodology or WEL for CNT fibres
- 0.01 fibres/cm³ for fibrous nanomaterials with high aspect ratios (<3:1 and length >5 µm) (BSI 2007)

Results- CNT manufacturing



PBZ sampling - respirable head d_{50}<4 µm AED during CNT synthesis and material recovery

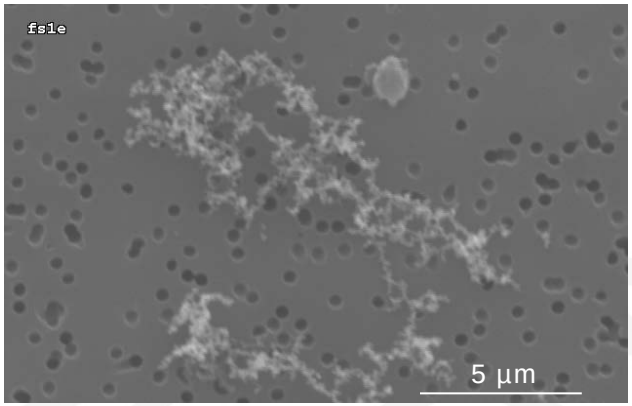


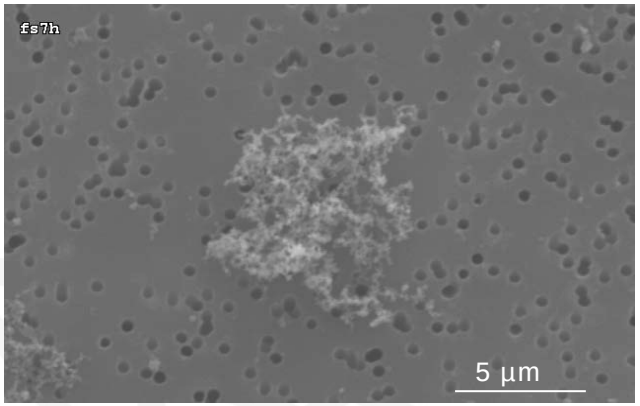


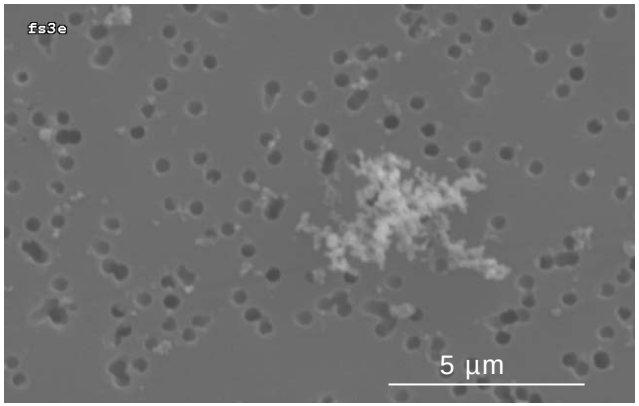
Nano-ID – sampling stage 0.5-1.0 µm

- Respirable fibres physical size >10 µm
- Equivalent EC samples below detection limit

Results- Production of nanocomposites







Site 1 - C-based aggregate particles from combustion sources and no evidence of CNT release

- Equivalent EC samples registered EC concentrations above REL
- Combustion sources likely the predominant source of elemental carbon

Sites 2 & 3 – nanocomposite production – no CNT release detected and EC below detection limit

Results- summary

Activities	Site	CNT detection	
		EC analysis	SEM analysis
CNT Manufacturing, recovery and testing	1	X	Y
Production of nanocomposites	1	Y	X
	2	X	X
	3	X	X

= False negative

= False positive

EC results alone suggest that the REL for CNT was not exceeded due to CNT release; SEM suggests a release- but is at an acceptable level?

Objective: Based on evidence gathered during the assessment provide recommendations for safe working to minimise exposure

Conclusions

EC measurement as a method to estimate workplace exposure to airborne nano-carbon materials:

- REL – used by companies in isolation to control exposure but not CNT & CNF specific
- Mass-based method- challenges for estimating releases of CNT & CNF - link between REL and toxicological effects
- Assessing exposure to CNT & CNF should involve a multi-metric approach- concurrent electron microscopy analysis to confirm the presence of CNT & CNF
- EC alone may be used to monitor specific environments where it has been demonstrated that a correlation exists with CNT & CNF exposure

Reduce workplace exposures to CNT & CNF as far as reasonably possible

Thank you!
Any questions?

Acknowledgements:

UltraWire

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http://ultrawire.eu/

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