EXPOSURE TO GRAPHENE IN A PRODUCTION PILOT PLANT

C. Vaquero[1], R. Wendelbo[2], A. Egizabal[1], J. López de Ipiña[1], C. Gutierrez-Cañas[3],

(1) TECNALIA, PTA-Miñano (Álava), 01510 Spain
(2) Abalonyx AS, Forskningsveien 1, 0373-Oslo, Norway
(3) University of the Basque Country, Alameda de Urquijo s/n,Bilbao48013,Spain

tecnalia Inspiring Business

nanoSAFE'18

Outline

- H2020 FAST Project – an overview
- Nanosafety-Strategy followed
- Results
- Conclusions

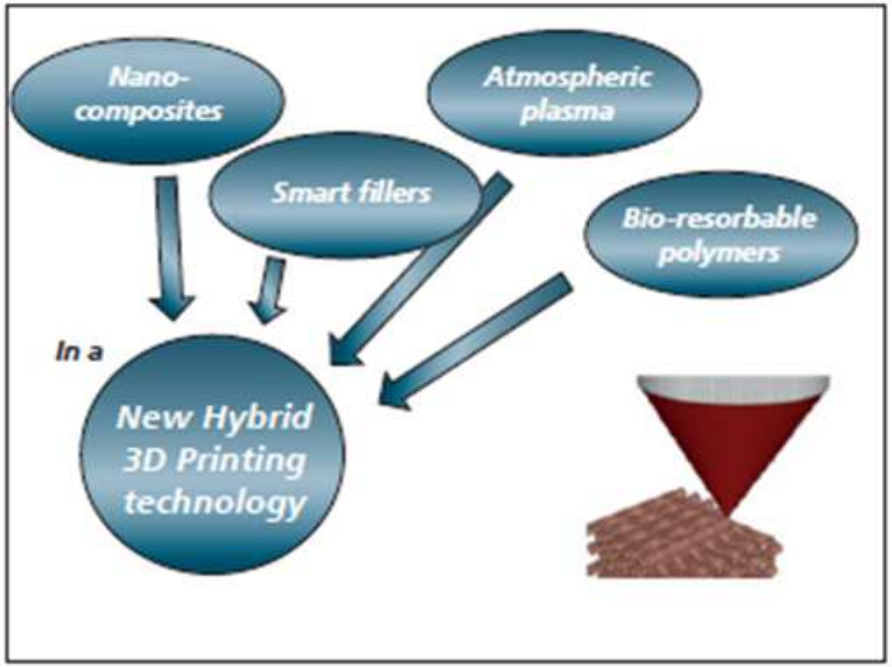
FAST
Functionally graded Additive Manufacturing scaffolds by hybrid manufacturing

The FAST project aims to make a new 3D printing technology available for the manufacture of implants customized to the patient at affordable cost.

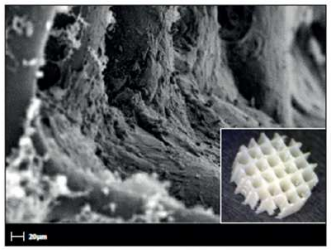
The picture below shows technology fields of importance in **the FAST project.**

Nanosafety assessment- integrated in all process steps

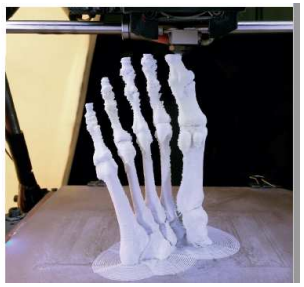
This work: focused in monitoring worker exposure during graphene synthesis in a pilot plant .



„Ingredients" of the FAST technology | © Padova University



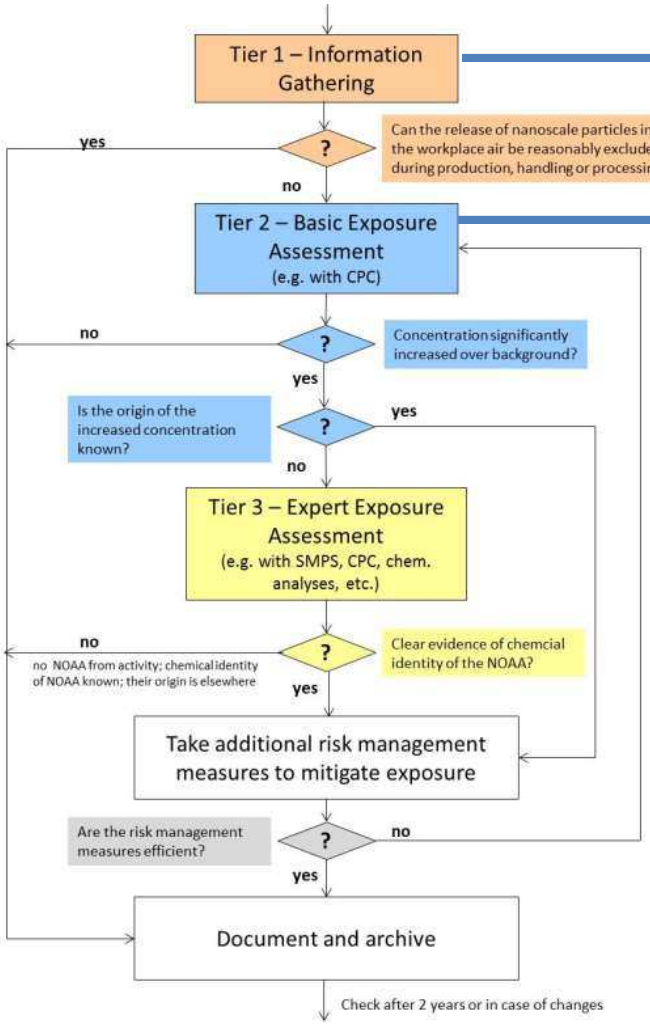
Scanning electron microscope image of cells adhering on a test scaffold surface © Maastricht University



tecnalia Inspiring Business

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 646155 .

Nanosafety-Strategy followed



* Info gathering
* Identification of workers exposure scenarios
* Qualitative risk assessment: Control Banding tools

* Quantitative assessment: measurements in the workplace

Strategy for exposure assessment following OECD (2015)

OECD (2015) Harmonized Tiered Approach to Measure and Assess the Potential Exposure to Airborne Emissions of Engineered Nano-Objects and their Agglomerates and Aggregates at Workplaces, 2015

I-Tier I-Information gathering

HAZARD:

- Collection of toxicology data:
  Limited information showed the potential behavioral, reproductive, and developmental toxicity and genotoxicity of graphene-based nanomaterials; **data are still very limited**, especially when taking into account the many different types of graphene-based nanomaterials and their potential modifications (Makoto et al, 2017).

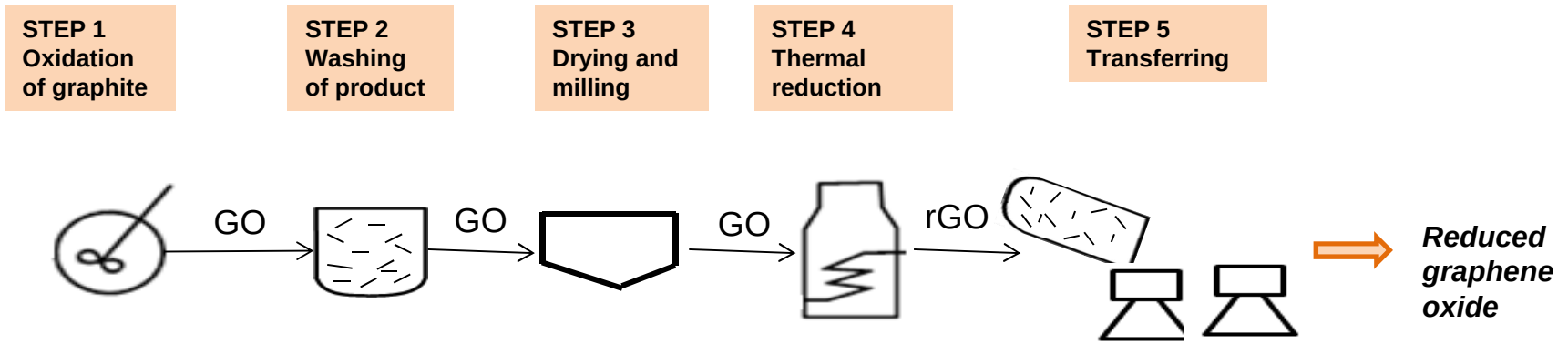
- Identification of Occupational Exposure Limits, OELs:
  No specific limits for graphene have been found. A categorical approach can be followed.

Nanomaterial	Specific approach	Categorical approach	Source
Graphene	Not found	NRV: 40000 #/cm3	van Broekhuizen, 2012
		BEL: 0.066 * WEL = 0.165 mg/m3 (OEL-TWA for graphite is 2.5 mg/m3)	BSI PD 6699-2:2007

Makoto et al, 2017. A review of toxicity studies on graphene-based nanomaterials in laboratory animals

I-Tier I-Information gathering

- EXPOSURE:
  Analysis of processes and identification of potential occupational exposure scenarios



I-Tier I-Information gathering

QUALITATIVE RISK ASSESSMENT: CONTROL BANDING TOOLS: to identify key exposure scenarios; using recognized control banding tools: Stoffenmanger nano (1), CB Nanotool (2)

				Stoffenmanager			CB nanotool			
Task		Form	Control used	HB	EB	RB	HB	EB	RB	Controls- recommended
T1	Oxidation	Dispersion (~kg/day)	Closed reactor + LEV	D	2	II	Medium	Extremely Unlikely	RL1	General ventilation
T2	Washing	Dispersion (~kg/day)	LEV	D	1	II	Medium	Extremely Unlikely	RL1	General ventilation
T3	Drying & Milling	Powder (~g/day)	Fume hood	D	1	II	Medium	Likely	RL2	Fume hood or LEV
T4	Thermal reduction	Powder (~g/day)	LEV	D	2	II	Medium	Likely	RL2	Fume hood or LEV
T5	Transfer	Powder (~g/day)	Fume Hood (+special device)	D	1	II	Medium	Likely	RL2	Fume hood or LEV
	Cleaning	Powder	Fume hood/LEV	D	n.a.	n.a.	Medium	Likely	RL2	Fume hood or LEV

- Exposure band (EB): is classified as “Low/extremely unlikely” when working with dispersions; they are “Likely” when handling powders.
- Hazard band (HB): is classified as “D: very high” (Stoffenmanger) and “Medium” (CB-Nanotool)
- Risk band: MEDIUM= HB x EB
- Engineering controls implemented: are in agreement with the recommended ones

(1) https://nano.stoffenmanager.nl/
(2) CB NanoTool (http://www.controlbanding.net/Home.html)

II-Tier II-Basic exposure assessment

METHOD

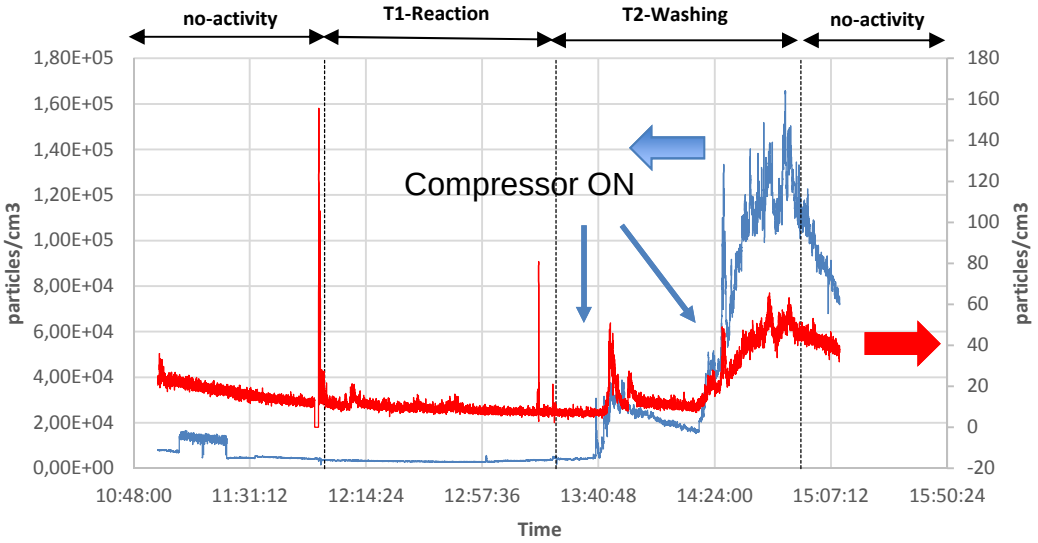
The OECD (2015) recommends to measure the potential release and exposure to engineered nano-objects using simultaneously on-line measurement devices and filter based sampling for off-line analysis.

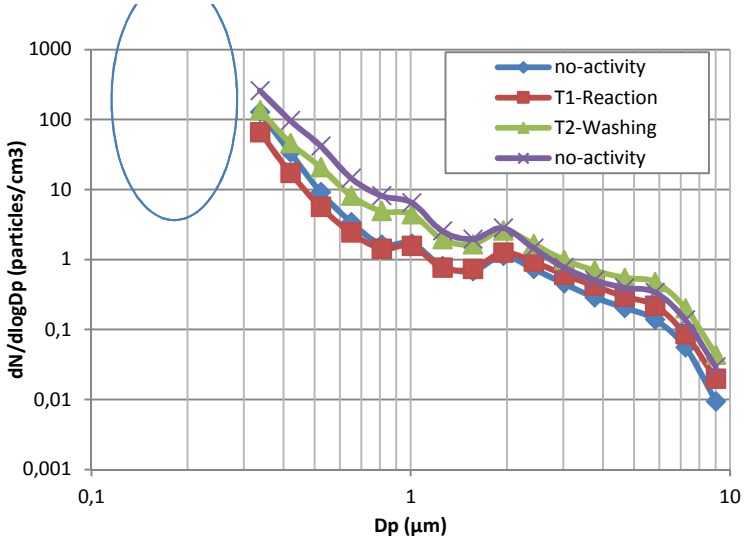
- **Two on-line devices** have been used to monitor the particle number concentration and to identify potential releases of particles to the workplace:
  - TSI CPC3007 (4 nm- 1 µm):
  - TSI-OPS3330 (0.3-10 µm):
- **Filter based samples** were collected for (1) gravimetric analysis, (2) elemental carbon analysis and for (3) SEM/EDX (MEB Quanta 200-FEI) to analyze the morphology of the particles released.
  - Gravimetric analysis: total aerosol mass (following NIOSH 0500).
  - Elemental carbon analysis (following NIOSH 5040).

II-Tier II-Basic exposure assessment

Day 1: Reaction & washing

- Significant release of particles during T2-washing
- Particles size < 300 nm
- The increase in concentration is coincident with the compressor-ON





II-Tier II-Basic exposure assessment

Day 1: Reaction & washing

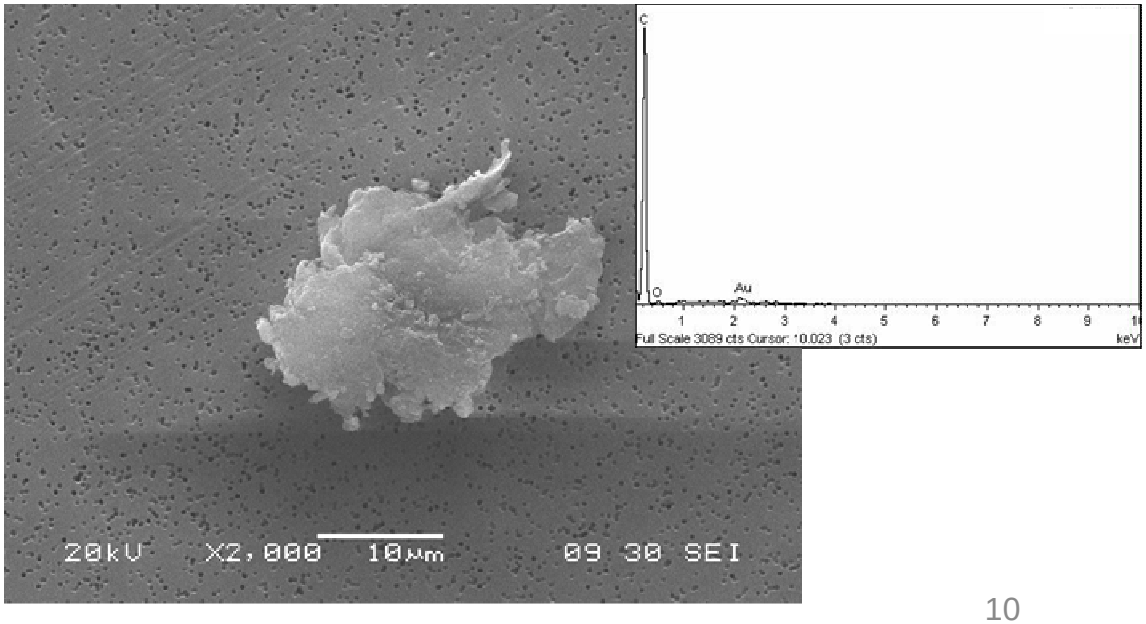
Task	Sampling time (min)	Sampling point	Q (lpm)	Volume (m3)	Elemental Carbon (mg)	Concentration (mg/m3)	8 hr TWA (mg/m3)
Background	67	in the lab	2.5	0.1675	< 0.001	< 0.006	< 0.0008
Reaction & Washing	188	at source	2.5	0.47	< 0.001	< 0.002	< 0.0008

<< 0.165 mg/m3

Elemental carbon analysis: EC concentration in the filters was below the limit of detection (LOD is 1 µg in the filter) 8 hr TWA elemental carbon concentration was < 0.0008 mg/m3, which is quite below the exposure limit considered for graphene.

SEM analysis:

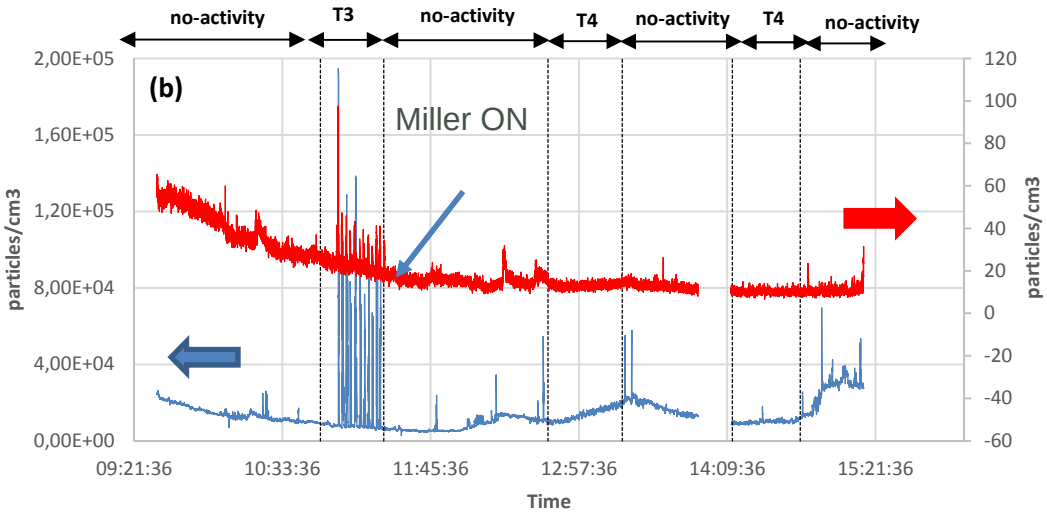
- Few particles deposited, most of them common ambient particles
- Few particles of carbonaceous nature were also identified: the figure shows a particle which EDX suggests a graphite particle around 30 µm.

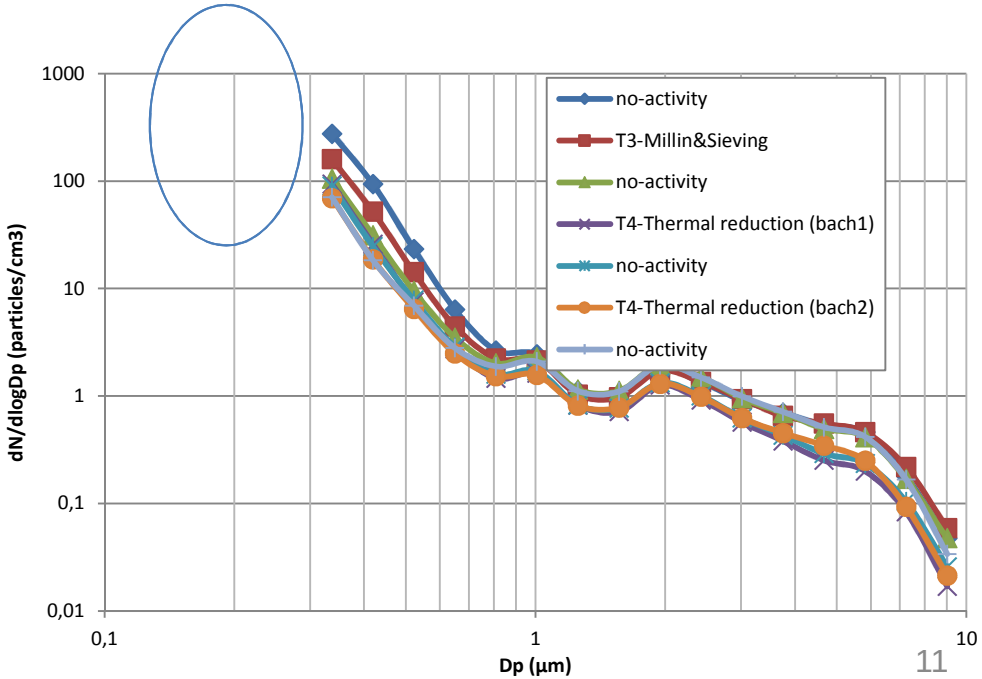


II-Tier II-Basic exposure assessment

Day 2: Milling & Thermal reduction

- High peaks of particle concentration during T3-milling & sieving
- Particles size < 300 nm
- The increase in concentration is coincident with the miller-ON





II-Tier II-Basic exposure assessment

Day 2: Milling & Thermal reduction

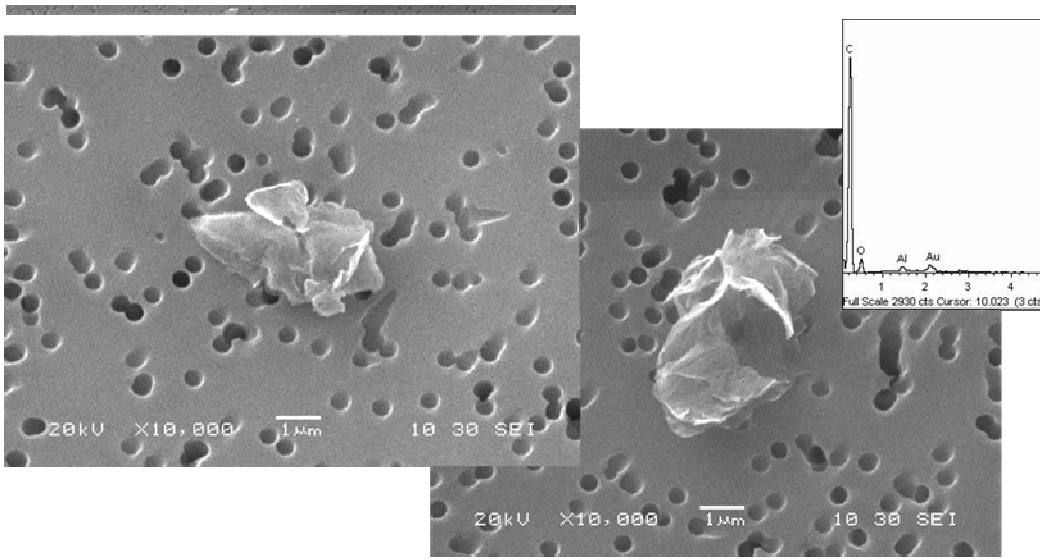
Task	Nº	Sampling time (min)	Sampling point	Q (lpm)	Volume (m3)	Total Mass (mg)	Concentration (mg/m3)	8 hr TWA (mg/m3)
Background	11	67	in the lab	2.5	0.1675	< 0.001	< 0.006	< 0.0008
Personal	12	148	PBZ	2.5	0.37	< 0.001	< 0.003	< 0.0008
T3: Milling ¬ Sieving T4- Thermal reduction	17	148	at source	2.5	0.37	< 0.001	< 0.003	< 0.0008

<< 0.165 mg/m3

Elemental carbon analysis: EC concentration in the filters was below the limit of detection (LOD is 1 µg in the filter)
8 hr TWA elemental carbon concentration was < 0.0008 mg/m3, which is quite below the exposure limit considered for graphene.

SEM analysis:

- Few particles, most of them ambient particles;
- More carbonaceous particles have been identified. Next figure shows several particles of layered rGO, flakes are several micron-size.



tecnalia Inspiring Business

Conclusions

- On-line devices reported significant release of particles during T2-Washing and during T3-Milling & Sieving; particles released were < 300 nm. It is suggested that the released particles are engine generated nanoparticles, from the compressor and the miller.
- SEM analysis identified graphite particles and aggregates of graphene flakes; these particles are in the micro range.
- Elemental carbon analysis showed that the concentration of elemental carbon was below the LOD (detection limit) of the analytic technique.
- The 8 hr TWA elemental carbon concentration was quite below the OEL (Occupational Exposure Limit) selected for the graphene.
- The Safe-by-Design approach underlines that safety should be considered in an integrated way right from the earliest phases of the research and innovation process. Safety is a key issue during scaling up the production.

FAST

Functionally graded
Additive Manufacturing scaffolds
by hybrid manufacturing

Thanks very much !!

celina.vaquero@tecnalia.com

Results of this work were funded by the European Union's Horizon 2020 research and innovation programe under grant agreement No 685825.

http://project-fast.eu

nanoSAFE'18

tecnalia Inspiring Business

This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 646155 .