# Strategies and Methods to Assess Occupational Exposures to Engineered Nanoparticles: NANODEVICE Contribution

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Finnish Institute of Occupational Health

Nanosafety Research Centre

# Shortage of knowledge on toxicological and ecotoxicological effects of ENP

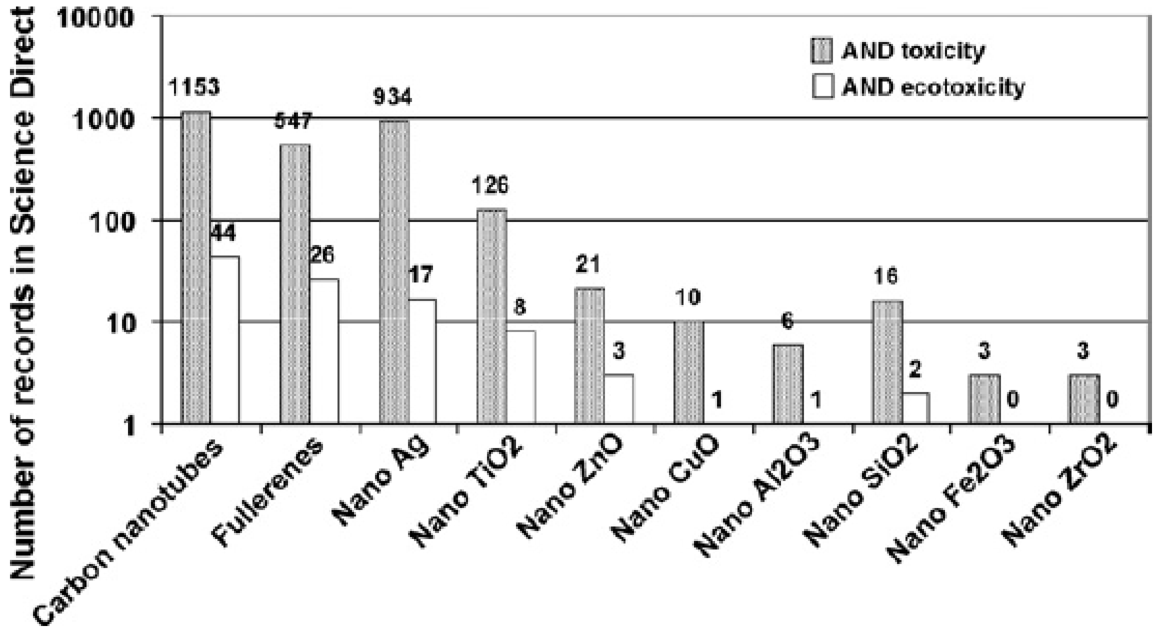



**Fig. 2.** Availability of data (number of records) concerning toxicological and eco-toxicological effects of various nanoparticles. Search was made in Science Direct; March 11, 2009 (all fields). For silver nanoparticles the search was made in April 4, 2009. "AND" means combination of the respective keywords.

*A. Kahru, H.-C. Dubourguier / Toxicology 269 (2010) 105–119*

# ENP workplace monitoring studies - almost complete lack of data

**Table 1**
Summary table of identified workplace air monitoring studies for manufactured nano-objects.

| Study # | Year | Authors | MNM | Facility | Activities |
|---|---|---|---|---|---|
| 1 | 2004 | Maynard et al. | SWCNT | Production (research scale)<br>Laboratorium | Removing CNT from production vessel<br>Agitation of CNT by vortex |
| 2 | 2004 | Kuhlbush et al. | Carbon black | Production (commercial scale) | Packaging/bag filling |
| 3 | 2006 | Kuhlbusch and Fissan | Carbon black | Production (commercial scale) | Reactor area Pelletizing area |
| 4 | 2008 | Yeganeh et al. | Fullerenes | Production (commercial scale) | Scooping, brushing, sweeping |
| 5 | 2008 | Fujitani et al. | Fullerenes | Production (commercial scale) | Bagging |
| 6 | 2008 | Han et al. | MWCNT | Production (research scale) | Recovering CNT; blending composites |
| 7 | 2008 | Bello et al. | CNT | Production (research scale) | Removal and detaching of CNTs |
| 8 | 2008 | Demou et al. | Metal-based | Production (pilot scale) | Reactor maintenance and cleaning, powder handling and packing, workplace cleaning |
| 9 | 2008 | Methner | Metal | Production (pilot scale) | Reactor cleanout |
| 10 | 2009 | Peters et al. | Lithium titanate Me-oxide | Production (Commercial scale) | Bagging, milling, powder sifting, loading dock |
| 11 | 2007 | Methner et al. | Carbon nanofibres | Research scale production of polymer composites | Chapping CNFs, transferring; mixing. Cutting composite |
| 12 | 2008a | Tsai et al. | Metals | Research | Transfer, pouring |
| 13 | 2008b | Tsai et al. | Aluminum oxide | Research | Compounding of Nanocomposites |
| 14 | 2009 | Bello et al. | CNT composites | Research | Machining (dry and wet cutting/band-saw/rotary cutting wheel) |
| 15 | 2009 | Vorbau et al. | Coating mixed with zinc oxide dispersion | Research | Abrasion test |

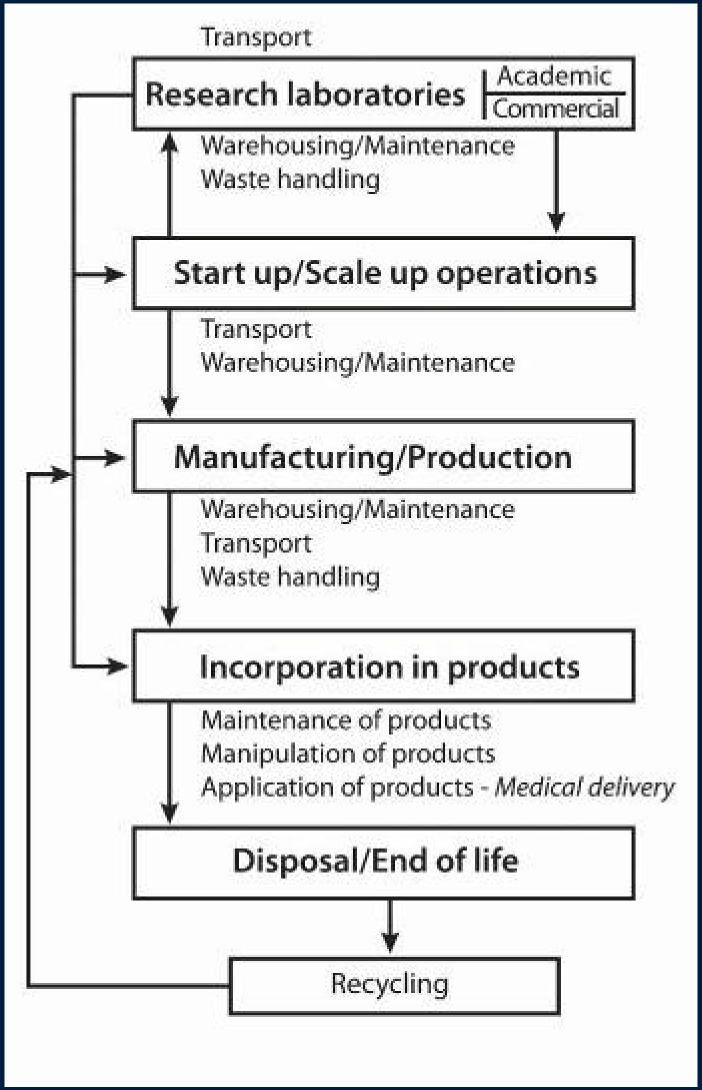
CNF, carbon nanofibre; CNT, carbon nanotubes; Me oxide, metal oxide; MWCNT, multiwall carbon nanotubes; SWCNT, singlewall carbon nanotubes.

*D. Brouwer / Toxicology 269 (2010) 120–127*

| process | characterization | |
|---|---|---|
| emission | Emission rate | |
| transmission | Environmental/ workplace concentration | |
| immission | Micro-environmental/ concentration | |
| exposure | Exposure concentration,.ie. Size fractionalized/ time-integrated BZ concentration | |
| intake | | Outer exposure surface |
| | Intake dose | |
| uptake | | Inner exposure surface |
| | Uptake dose | |
| Distribution | | |
| Metabolism | Biologically relevant dose | |
| Excretion | Target dose | |

# Range of workplaces that could involve exposure to ENM

Schulte P et al, Sharpening the focus on occupational safety and health of nanotechnology. SJWEH (2009)

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# Development of ENP exposure monitoring instruments, new monitoring strategies in workplaces: NANODEVICE approach

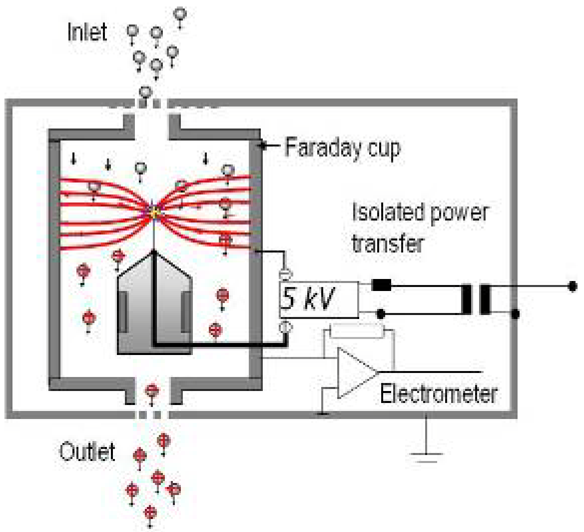
- Three approaches: (up to 20 instruments)
  - existing principles, affordable close-to-the-market on-line monitors
  - Amending current measurement principles, affordable on-line measurement devices
  - remote from the market instruments, novel measurement concepts, new metrics for ENP exposure (aerosol reactivity)
- Laboratory assessment and field testing of the novel devices

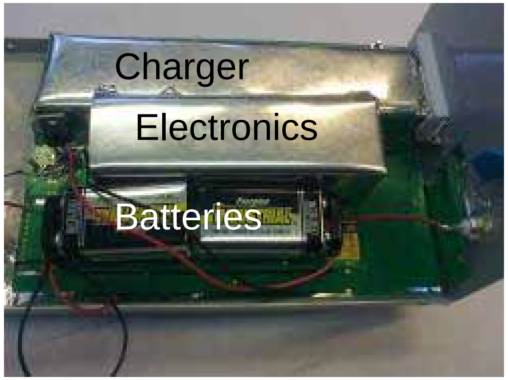
# Impact of NANODEVICE on Measurement Strategy

| ‘Nano specific’ exposure issues | Current drawback | NanoDevice deliverable |
|---|---|---|
| Coagulation processes / interaction with background aerosols occur during transport to worker after emission | No device/ samplers for Breathing Zone concentration | -Variety of personal samplers/ monitors and portable sensors<br>-Modelling of coagulation/ interaction processes for workplace scenarios |
| No agreement on (health-) relevant exposure/ dose metric | Suit of devices needed to address all exposure metric | -Integrated/ modular system to monitor particle concentration, surface area concentration + sampling<br>- Surface area concentration screening device |
| Identification of MN-objects key factor for background distinction | MNO-specific monitors lacking<br>Sampling + off-line analysis (chemical/ EM) needed | -Specific monitors e.g. for nano-fibers<br>-Size-selective (pre-selection-multi-stage) samplers<br>Detection system (/ sensors) for deposited particles |
| Gap between exposure monitoring and health- effects | (health-) relevant exposure assessment methods are lacking | -Modification of (personal) sampler for cell exposure<br>-catalytic and surface-chemical aerosol monitoring |

# Portable active surface area monitor

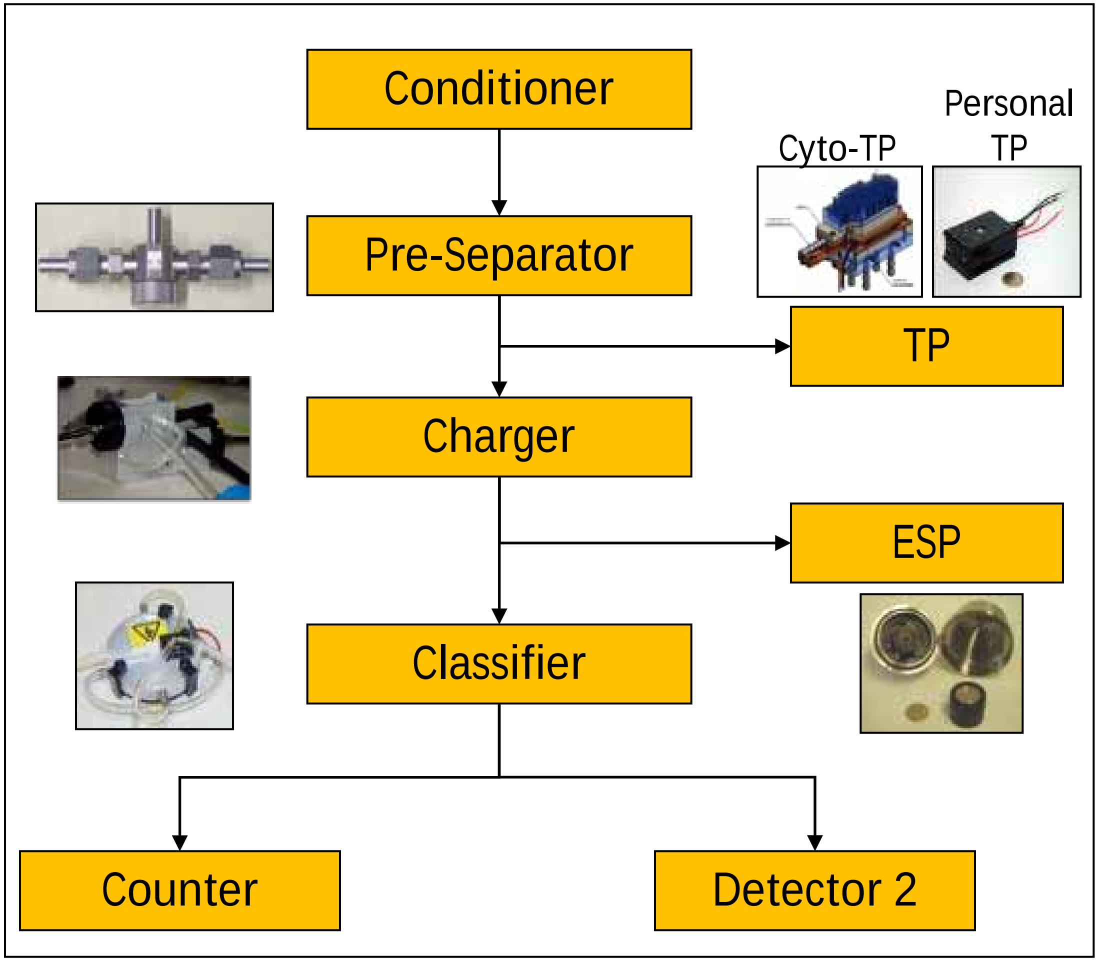
- Partners: Dekati and Tampere University of Technology
- Main target: Low Cost Nanoparticle Sensor
- Escaping charge technology
  - Particle charging with corona discharge
  - Electrical detection of charged particles with sensitive electrometer
  - Detection of particles (electrical charge) flying out from the system, ”escaping charge measurement”
  - Flow-through design, no collection of particles
  - Low pressure drop, fan operated
- Single board sensor design
  - Charger, electrometer and high voltage  power supply integrated to a single electronics board
  - Battery operated
- ”Fire-Alarm” –type device
  - ”Green, Yellow, Red” indicators
  - Low cost
- Workplace monitoring, NOT a personal sampler




*Prototype system on a single PCB board*

# Size-discriminating number & surface area aerosol monitor & sampler




- Conditioning (rh, T) and removal of large (>450 nm) particles
- Unipolar diffusion charging
- Classification by electrical mobility
- Detection of size independent (number) and size dependent concentration for morphology dependent information à indication for presence of ESP
- Parallel collection of particles for consecutive chemical & morphological analysis for definitive proof of presence or absence of ENP; long-term sampling with thermal precipitator (TP), short term sampling with electrostatic precipitator (ESP)
- Collection directly onto cells for tox. analysis with Cyto-TP

# Naneum Limited

Device 1. Naneum has developed "a *wide range, size resolving personal sampler* for collecting *in-situ* ENP in the size range 1 nm – 300 nm

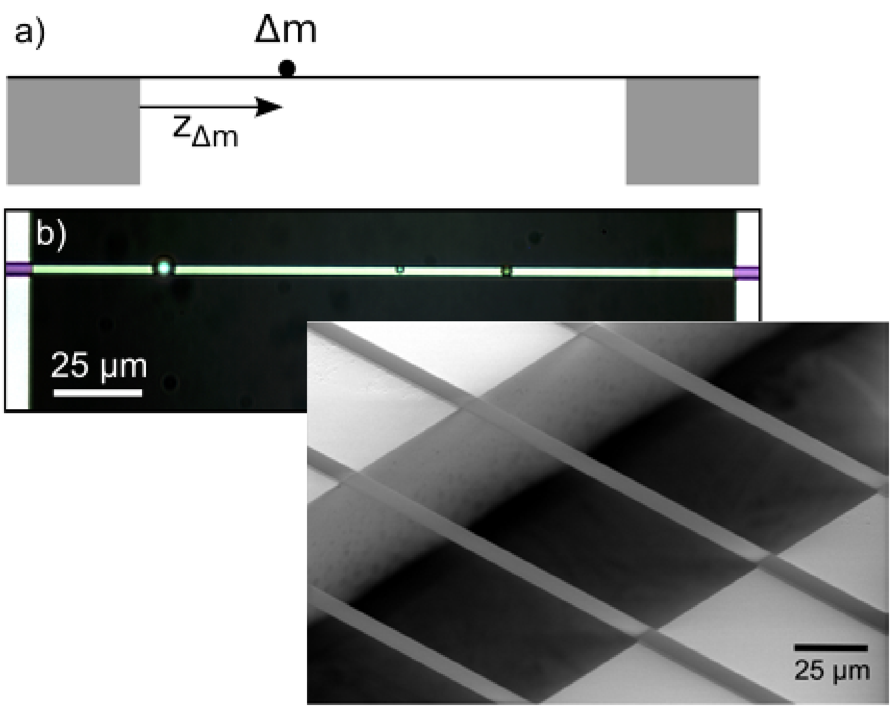
| Stage | Dmin, nm | Dmax, nm |
|---|---|---|
| 1 | 1 | 1.5 |
| 2 | 1.5 | 5 |
| 3 | 5 | 15 |
| 4 | 15 | 60 |
| 5 | 60 | 300 |

Device 2. Naneum is developing a novel instrument for detecting ENP such as Carbon Nanotubes (CNT) and potentially other nano-objects, on-line *in-situ* and against normal background atmospheric aerosols. A prototype device has been constructed and preliminary trials have successfully demonstrated proof of concept.

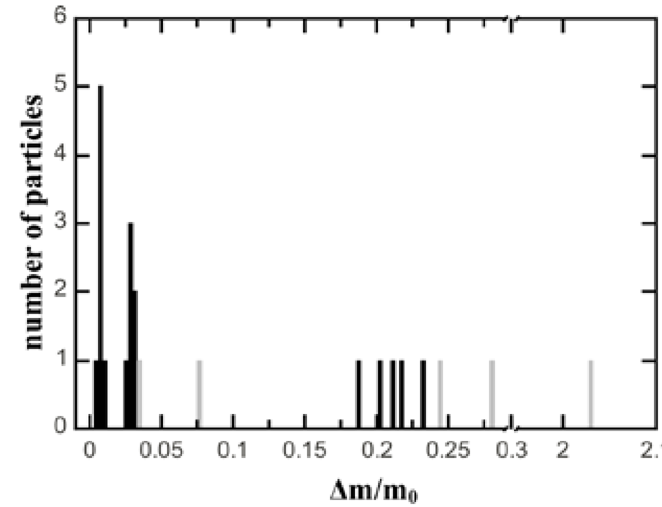
Technical University of Denmark

Device: Micro sensor based particle mass spectrometer

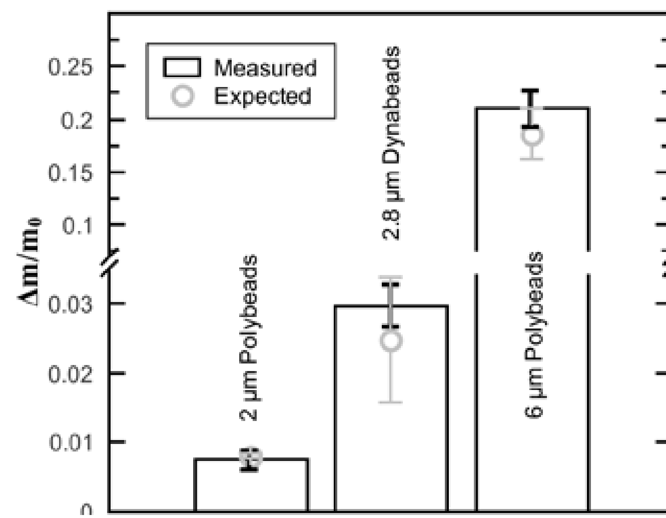
Principle: Resonant frequency shifts due to particles landing on string.
Mass of individual particles can be calculated by measuring the frequency shifts of the first two bending modes.




Histrogram of mass ratio for 3 different particle types.
(particle mass $\Delta m$, string mass $m_0$)




Comparison of measured vs. expected particle mass.



# Calibration & Testing

- Calibration
  - Nano Test Facility
    large wind tunnel + sedimentation chamber with various aerosol generators for soot, NaCl, $TiO_2$.
    Parallel Measurements against state-of-the-art devices, eg. SMPS, ELPI etc
  - Caiman – lab system: Pallas Generator with control on morphology of NP
  - Calibration tool for particle number concentration based on the principle of coagulation

- Testing in the field
  - Project internal field teams and external technicians will test the new devices in companies
  - ease-of-use ?
  - Comparison to competion on the market

## Summary

- Need to understand ENP behavior to define an appropriate exposure assessment strategy
- Need for novel technologies to assess exposure to ENP on-line with a potential to separate between background NP and ENP – needed for OELS, other limit values
- New monitoring innovations are an important prerequisite to promote nanosafety
- Existing gap in exposure data is now being filled with the ongoing research on novel monitoring technologies, and is supported by the promotion of standardization activities

# SENN2012

Join us in the next step of
the nanosafety discussion!

**SENN2012**

International Congress on Safety of Engineered Nanoparticles and Nanotechnologies

28-31 October 2012, Helsinki, Finland

**www.ttl.fi/senn2012**

Finnish Institute of Occupational Health

The goal of the SENN2012 Congress is to summarize and share the latest knowledge regarding the safety of engineered nanomaterials and nanotechnologies.

This meeting is a must for those dealing with nanosafety issues in:

**materials science**
**measuring technologies**
**risk assessment and risk management**
**health, toxic effects**
**standardization**

The Congress arrangements are funded by the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement no. 211464.

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**Thank you!**

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