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Measurement of exposure to inhaled nanoparticles in the workplace

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Background



• Royal Decree of 11/03/2002 (next speaker)

Law concerning the health protection and safety of workers against the risks of chemical agents at the workplace.

• Article 8

Employers are obliged to ensure the protection of the health and safety of workers from the risks related to hazardous chemical agents at work. Duty of employers to carry out a Risk Assessment whenever chemical agents are handled during work activities, including MNM.

• Key part of any risk assessment is a thorough understanding of the exposure potential for workers.



Exposure Potential

Two approaches to derive nanoparticles exposure potential in workplaces:

1. Studies in **real** workplaces

+ Data from real work conditions

- Interference of background aerosol



- 2. Process based studies in **simulated** workplaces and of simulated work processes.
 - + No background aerosol present
 - + Variation in handling/conditions influence release rates
 - No real workplace





Nanoparticle Exposure Metric in Air (1)

- » Current method assessing worker exposure to airborne particles in the workplace involves the measurement of mass concentration of health-related fractions of particles in the worker's breathing zone.
- » Nanoparticles generally contribute negligibly to the integral mass concentration of the inhalable or respirable dust fraction.
- Most relevant metric relating dose to the observed biological fate, behaviour, and health effects of a specific nanomaterial not determined
- » In 2007 Maynard and Aitken addressed the issue of exposure metrics
 - Aerosol number concentration
 - Aerosol surface area
 - Aerosol mass concentration



» Advice to determine as many metrics of the exposure as possible

Maynard AD, Aitken RJ., Assessing exposure to airborne nanomaterials; current abilities and future requirements. Nanotoxicology 1:26-41. (2007)



Nanoparticle Exposure Metric in Air (2)

CEN/TC 137 - WG3 Particulate matter

<u>Guideline under development</u>: Workplace Exposure - Metrics to be used for the measurements of exposure to inhaled nanoparticles (nano-objects and nano-structured materials) such as mass concentration, number concentration and surface area concentration

- Guidance for choosing the correct particle metric during a basic and comprehensive assessment
- Presentation of operation, (dis)advantages of various techniques measuring these metrics





Nano Aerosol Monitors/Samplers (1)

Monitors measuring **particle number concentration**:

- 1. Condensation Particle Counter (CPC)
- 2. Diffusion Charging Instrument (DC)



Nano Aerosol Monitors/Samplers (2)

Monitors measuring **particle surface area**:

Diffusion Charging Instrument (DC)



Bloor





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Alveol

Nano Aerosol Monitors/Samplers (3)

Samplers for determining nanoparticle mass (chemical element):

Aerodynamic collection

Cyclones for respirable fraction – PM1

- Cascade impactors (last stages 10-300 nm)
- Diffusive collection (thermophoretic/electrostatic)

Analytical:

- All : ICP-MS/PIXE/Raman
- Individual: TEM/SEM EDX/EELS









Nano Aerosol Monitors/Samplers (4)

Monitors measuring size resolved nanoparticle number concentration

- Electrical Mobility equivalent distribution
- Aerodynamic equivalent distribution



Measurement Strategy (1)

Exposure assessment of nano aerosols in the workplace, need for:

- » globally harmonized approach
- » pragmatic, widely useable (SME and large companies)
- » limited resources

Development of a **stepwise or tiered procedure** for determining workplace exposures to nanomaterials

- 1. NanoGem www.nanogem.de/cms/nanogem/upload/Veroeffentlichungen/nanoGEM_SOPs_Tiered_Approach.pdf
- 2. INRS www.inrs.fr/dms/inrs/CataloguePapier/ND/TI-ND-2355/nd2355.pdf
- **3. Safework Australia** <u>www.safeworkaustralia.gov.au/sites/swa/about/publications/pages/measurements-particle-</u> emissions-nanotechnology-processes-with-assessment-measuring-techniques-workplace-controls
- 4. NEAT Mehtner et al 2010 J Occup Environ Hyg 7:3,173-132 (part A)/ J Occup Environ Hyg. 7:3,163-76 (Part B)
- 5. FP7 MARINA www.marina-fp7.eu/downloads/MARINA-MS5_Workshop_Report_20130418.pdf.zip
- 6. OECD SG8 ENV/CHEM/NANO(2014)12



Measurement Strategy (2)

CEN/TC 137 - WG3 Particulate matter

<u>Guideline under development</u>: Workplace exposure – Guidance document of assessment of exposure to inhaled manufactured nanoparticles

- Description of existing or recently developed tiered approaches regarding assessing inhalation exposure to nanomaterials
- Testing of the proposed decision rules in these tiered approaches.
- Generic tiered approach





Measurement Strategy (3)

Generic Tiered Approach





Measurement Strategy (4)

Tier 1 Initial Assessment – Release/Potential for exposure

Information gathering (desk & walkthrough survey):

- » Nanomaterials
- » Process & maintenance
- » Workers tasks
- » Sources of incidental/process particle emission
- » Exposure controls
- » Ventilation

<u>Measurements</u>

» CPC / OPC (identify points of particle emission)

Decision: whether or not release of NPs into workplace air can be excluded





Measurement Strategy (4)

Tier 2 Basic Exposure Assessment – Evidence of exposure

Simplified exposure measurements:

- » Limited number of easy to use instruments (CPC, miniDisc, nanoTracer)
- » Emission source during activity
- » Background levels (before/after activity) or nearfield/ far-field measurements
- » Sampling and chemical analysis (element and/or total)



Decision: Concentration level significantly increased over background



Measurement Strategy (4)

Tier 3 Comprehensive Exposure Assessment – Characterization of exposure

- » Collection of particles for off-line analysis
- » Particle morphology (SEM/TEM)
- » Chemical composition (SP ICP-MS, μXRF, ICP-AES)
- » Real time measurements (particle number, size, surface area, mass using CPC, FMPS, SMPS, NSAM, TEOM)

Decision: Take additional risk management measures to mitigate exposures (precautionary principle)





Nano Reference Values (1)

- » No Health based limit values have been defined yet
- » August 2010: Proposal for Nano Reference Values (NRVs) by the Social and Economic Council (SER) based upon the IFA concept (Broekhuizen et al, 2012)
- » Background corrected 8-h TWA exposure level.

Class	Description	Density	NRV (8-h TWA)	Examples
1	Rigid, biopersistent nanofibres for which effects similar to those of asbestos are not excluded	_	$0.01 \text{ fibres cm}^{-3}$	SWCNT or MWCNT or metal oxide fibres for which asbestos-like effects are not excluded
2	Biopersistent granular nanomaterials in the range of 1–100 nm	$>6000 \text{kg m}^{-3}$	$20\ 000\ \text{particles}\ \text{cm}^{-3}$	Ag, Au, CeO ₂ , CoO, Fe, FexOy, La, Pb, Sb ₂ O ₅ , SnO ₂
3	Biopersistent granular and fibre form nanomaterials in the range of 1–100 nm	$< 6000 \text{kg m}^{-3}$	40 000 particles cm ⁻³	Al_2O_3 , SiO ₂ , TiN, TiO ₂ , ZnO, nanoclayCarbon black, C ₆₀ , dendrimers, polystyreneNanofibres with excluded asbestos-like effects
4	Non-biopersistent granular nanomaterials in the range of 1–100 nm	_	Applicable OEL	e.g. Fats, NaCl

Table 3. NRVs for four classes of MNMs

SWCNT, single-wall CNT; MWCNT, multi-wall CNT.

Broekhuizen et al. Exposure Limits for Nanoparticles: Report of an International Workshop on Nano Reference Values. Ann Occup Hyg (2012) 56 (5): 515-524



Nano Reference Values (2)







21/04/2015 © 2014, VITO NV Broekhuizen et al 2012

Simulated work places or processes (1)

Nanoparticle release studies under laboratory conditions

- » Conditioning of the generated aerosol (e.g. dilution, neutralization)
- » Process control (e.g. avoidance of background concentration, particle contamination)

Requires encapsulation and purging with filtered air or gas





Simulated work places or processes (2)

Simulated treatment processes found in literature roughly divided into four classes according to NM state:

- 1. Powders (e.g. dustiness testing)
- 2. Suspensions (e.g. sonication, spraying)
- 3. Coatings (e.g. weak abrasion process, sanding)
- 4. Composites (e.g. cutting, drilling)







Simulated work places or processes (3)

Dustiness Testing for powders

- 2 reference methods in EN 15051:2013 (part 1-3) Workplace atmospheres. Measurement of the dustiness of bulk materials. (PM100, PM4)
 - Rotating drum method
 - Continuous drop method
- » CEN/TC 137 WG3: Technical Specification under development: Nanomaterials -Quantification of nano-object release from powders by generation of aerosols
 - 2 reference methods (NC + SD)
 - Vortex shaker (NC + SD)



Guidance documents / Reference



EC Employment, Social affairs and Inclusion published two guidance documents

- » offering an overview of the issues surrounding the safe use of MNMs in the workplace
- » setting out the broad outlines of preventive action
- » providing a practical tool for complying with specific aspects of ensuring workers' safety, such as risk assessment and risk management.

Working safely with manufactured nanomaterials - Guidance for Workers <u>http://ec.europa.eu/social/BlobServlet?docId=13088&langId=en</u> Working safely with manufactured nanomaterials - Guidance for Employers <u>http://ec.europa.eu/social/BlobServlet?docId=13087&langId=en</u>



Future work & Conclusions

- Continuation with harmonization & standardization for workplace and laboratory measurements
- Harmonization in data treatment and analysis, including statistics
- Workplace studies & laboratory simulation requires comparisons with reference activities, reference materials
- Describe nanomaterials and processes studied in sufficient detail
- Simultaneous measurement of multiple parameters
- Tiered approach most practical for workplace and laboratory measurements



Questions? Comments?





ENVIRONMENT HEALTH & SAFETY



