RISK MANAGEMENT MEASURES FOR NANOMATERIALS

To what extent does engineered and personal protection equipment reduce exposure to manufactured nanomaterials in the work environment?

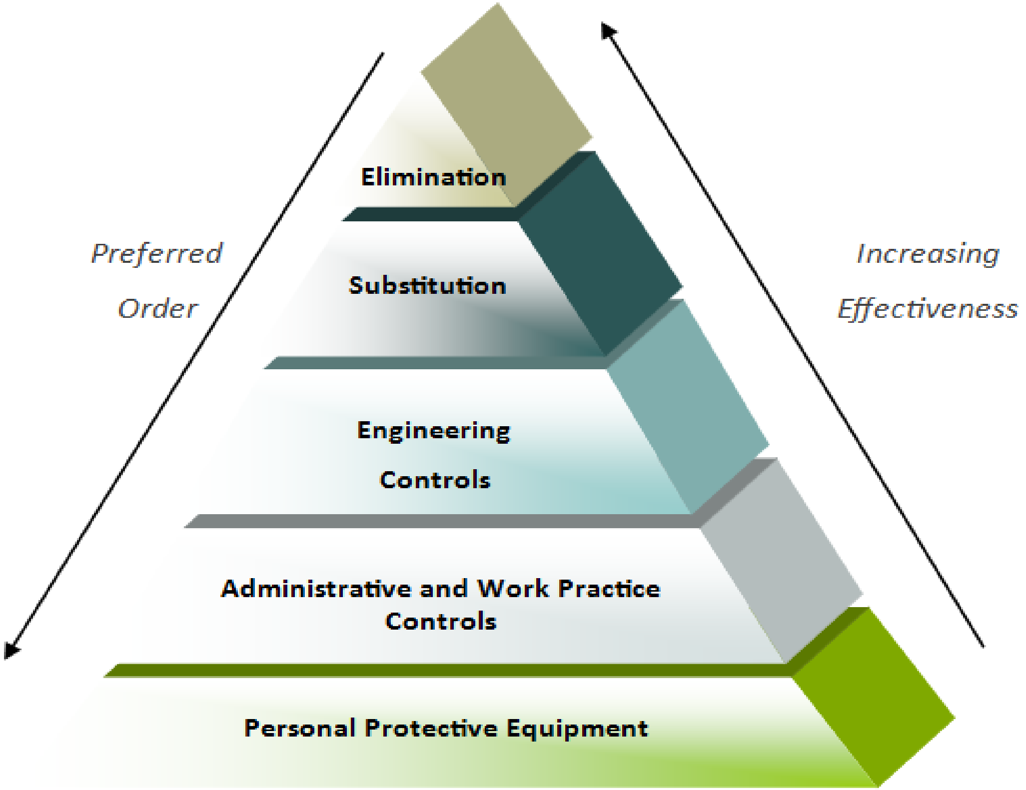
innovation for life

Wouter Fransman

EXPOSURE TO ENM

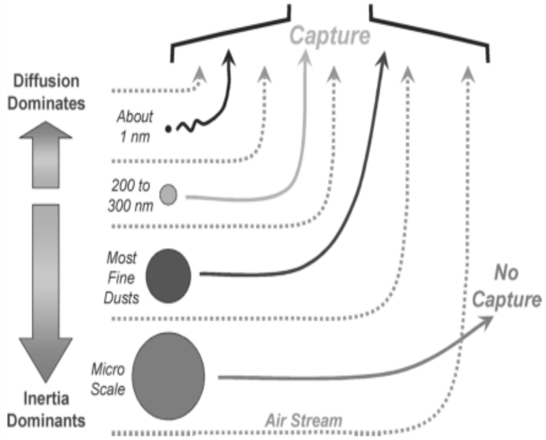
Emission Source	NPs Type	Measured levels range
Primary / SD1		
Liquid-phase reaction	PGNP	$4.0x10^4$ to $11.0x10^6$
Flame spraying	PGNP	$4.7x10^3$ to $1.0x10^6$
CVD	PGNP	Non-significant
Top-down (milling)	ENPs / PGNP	$3.0\ 10^3$ to $1.0x10^6$
Secondary NP aerosol / SD2		
Weighing of powders	ENPs	$2.0X10^4$ to $7.0x10^4$
Harvesting	ENPs	$2.0X10^4$ to $5.0x10^4$
Manual packaging (Bagging)	ENPs / PGNP	$20.0x10^4$
Bag emptying of powders	ENPs	Significant increase
Melt Blending	ENPs / PGNP	> $1.0x10^5$
SD3a / SD3b		
Spraying of liquid	ENPs	$2.0x10^8$
Spraying (gas)	ENPs	$1.6x10^5$ to $2.0x10^{10}$
Injection Molding	ENPs	> $8.0x10^5$
Brushing and rolling	ENPs	> $6.0x10^5$
Sonication of nanodispersions	ENPs	> $8.0x10^6$
Tertiary NP aerosol / SD4		
Abrasion of nanoproducts	PM / EMNP	$8.0x10^3$ to $2.0x10^4$
Drilling	PM / EMNP	$4.0x10^4$
Grinding	PM / EMNP	$3.0x10^3$ to $1.0x10^6$

HIERARCHY OF RISK MANAGEMENT MEASURES



SOME KEY PRINCIPLES

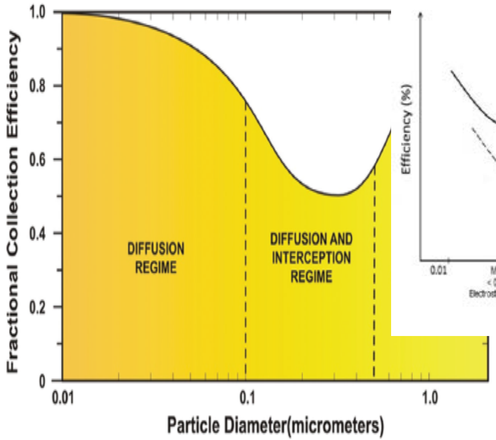
Ventilation

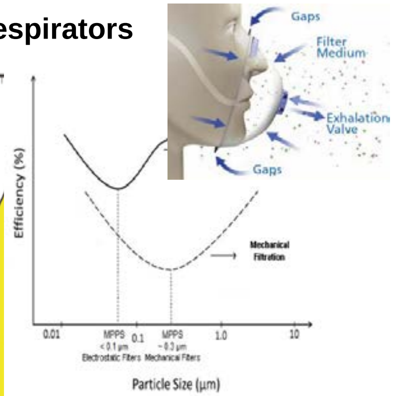


Schulte et al., 2008

For particles < 200nm diffusion dominates & capture efficiency expected to decrease

Respirators





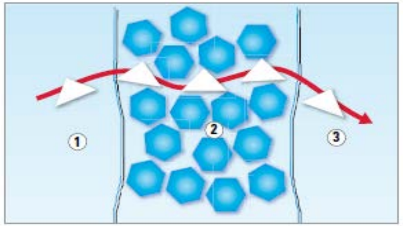
Bahloul et al., 2016

Lee and Liu, 1980

Small particles are bombarded by air molecules and cause particles to deviate from the airstream and trapped on filter media more efficiently *(single fibre filtration theory)*

Electrostatically charged filters increase the filtration efficiency

Clothing / gloves

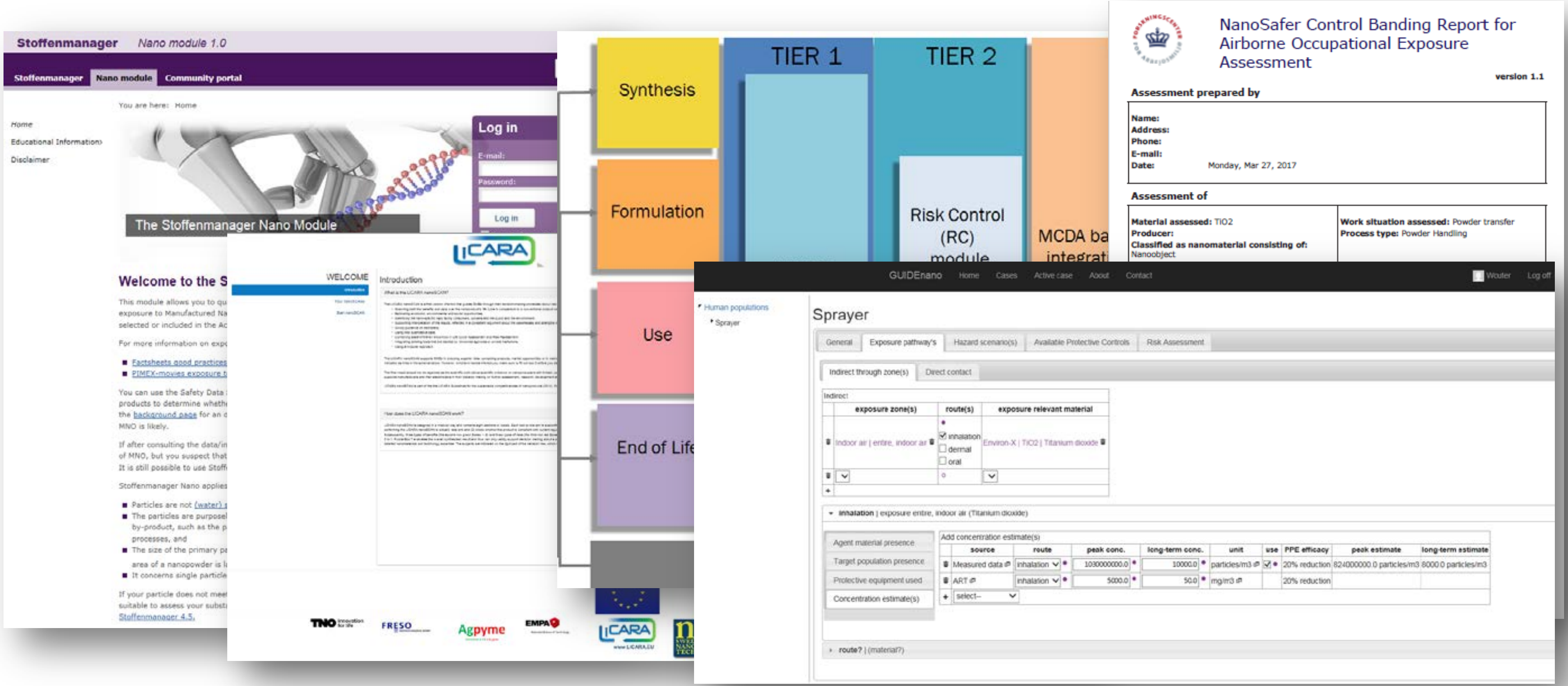


Normalized breakthrough time at a permeation rate of 1.0 µg/(cm²·min) in minutes	EN Class
> 10	1
> 30	2
> 60	3
> 120	4
> 240	5
> 480	6

* EN 14325: Protective clothing against chemicals - test methods and performance classification of chemical protective

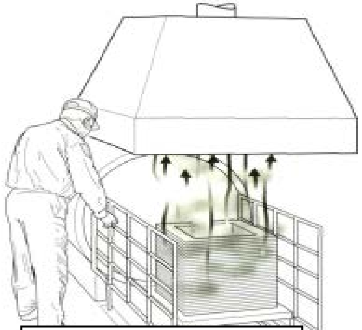
Nano-sized particles may under certain conditions more easily permeate and penetrate through some types of protective materials / textiles / fabrics

RMM FOR EXPOSURE / RISK ASSESSMENT



LOCALIZED CONTROLS

- Suppression techniques
  - Wetting at the point of release
  - Knockdown suppression
- Containment (non-extracted)
- Local ventilation systems
  - Receiving hoods
    - Canopy hoods (hot processes)
    - Other receiving hoods
  - Capturing hoods
    - Fixed
    - Movable
    - On-tool (integrated) extraction
  - Enclosing hoods
    - Glove box
    - Fume cupboard
    - LEV systems with partial enclosure (no front cover)

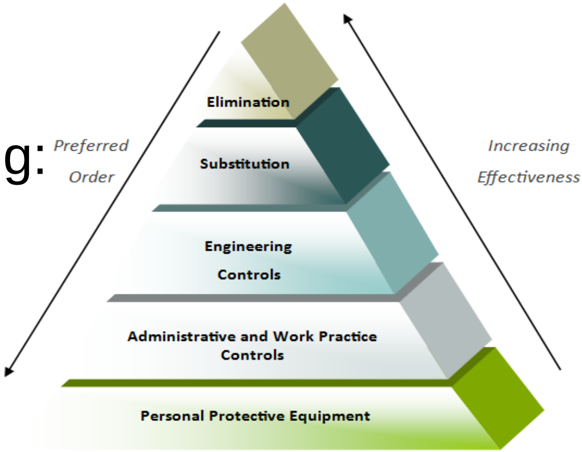


Efficacy = 0.5

Efficacy = 0.0001

REVIEW THE EFFICIENCY OF RMM

- Derive quantitative effectiveness values for modeling:
  - Differences in the effectiveness of RMM for nanomaterials versus conventional materials?
  - Adjust existing effectiveness values of RMM relevant for conventional substances? If so, what is the rationale and evidence we base these values on?



- Selected RMM:
  - Engineering controls
  - Respiratory Protective Equipment (RPE)
  - Skin Protective Equipment (SPE) – gloves and clothing

METHODOLOGY

- Review of published literature (2005 to 2016), incl. experimental studies performed in Guidenano (WP8) and other EU funded projects
- Derive conservative values for modelling purposes → 90% CI of the 5% percentile
- Evaluation included nano-specific and conventional data; and agglomerated / aggregated particles
- Considering all available information, incl. existing models, databases, experimental data, literature and regulatory bodies

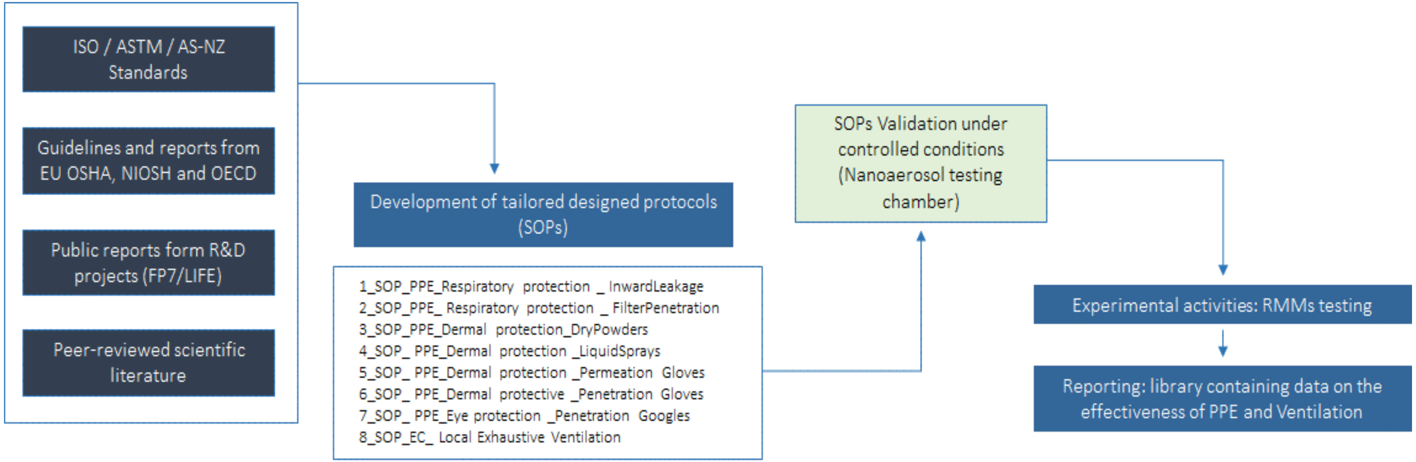
AVAILABLE DATA

RMM	Studies *(data points)**	Remarks
Engineering controls	12 *(75)*	o 10 types of controls *(based on ART categories)* o Range of NMs, e.g. TiO_2, CNT, SiO_2, graphene; mostly ˜5 to 560 nm tested o Cross-sectional & (semi-) experimental methods
Respiratory Protective Equipment	15 *(365)*	o 9 types of respirator types *(based on OSHA Regulation , 29 CFR1910)* o Mostly NaCl, also SiO_2, TiO_2, etc; <100nm (mono-/polydisperse) tested o Majority experimental studies, static or dynamic tests
Skin Protective Equipment - Clothing - Gloves	 7 *(163)* 2 *(31)*	o 7 types of protective clothing, 8 glove types *(based on Directive 89/686/EEC)* o Mostly NaCl, SiO_2, TiO_2, etc; gloves (colloidal aerosol 20-110nm); clothing (solid & colloidal aerosol 20-300nm) o Experimental, various test methods, static & dynamic

* *36 of the ˜90 pre-screened studies (incl. experimental data) could be used to derive quantitative effectiveness values*

RMM TESTING APPROACHES (SOPS)

- Evaluation of RMM effectiveness requires the definition of reliable, robust and reproducible testing approaches



DEFINITION OF TESTING APPROACHES (SOPS)

- ITENE exposure chamber prototype, developed within the EU NanoRisk and EU GuideNano.

- Validation of developed SOPs
- Development of experimental set-ups
- Protocols were revisited and when necessary, adapted to the limitations of the experimental tests.

A common European approach to the regulatory testing of nanomaterials

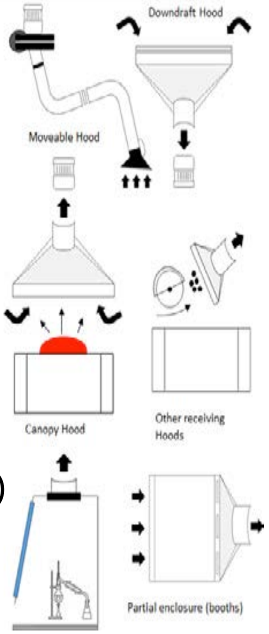
ENGINEERING CONTROLS

Control measure		Efficiency (%)		
		Nano dataset[A]	Proposed*	Specific sources[B]
Physical containment	Low to high level	*50 – 99.999*	**85-99.9**	ART/ECEL, Tsai et al., 2008/2012
Receiving hoods	Canopy hoods	-	**50**	ART/ECEL, Lo et al., 2012; Methmer et al., 2012
	Other receiving hoods	-	**80**	ART/ECEL
Capturing hoods	Fixed	*75 – 100*	**90**	Lee et al., 2007, Methmer 2008
	Movable	*46 – 97*	**50**	Methmer 2008, Frijns et al., 2016
	On-tool	-	**90**	ART/ECEL
Enclosing hoods	Fume cupboard	*57 – 95*	**90**	ART/ECEL; Tsai et al., 2008/9
	Horizontal / downward laminar flow booth, other	-	**90**	ART/ECEL
Glove bags	Non ventilated	-	**99**	ART/ECEL
	Ventilated or kept under negative pressure	-	**99.9**	ART/ECEL
Glove boxes	Low to high specification	*˜97–98 (n=2)*	**98 – 99.99**	ART/ECEL, Debia et al., 2013
Suppression techniques	Wetting at release point	*68 – 99*	**90**	ART/ECEL, Bello et al., 2009
	Knockdown suppression	-	**30**	ART/ECEL

* Proposed value based on all sources
A Based on reviewed nano dataset (min-max)
B Specific sources that determined the proposed value

ENGINEERING CONTROLS

- Generally, very small datasets available. Most data on fixed capturing hoods (n=26).
- Deviations from existing values (of conventional substances) as proposed by ART/ECEL include:
  - More conservative values for containment (85 – 99.9%) considering increased diffusion and escape of NPs
  - Fume cupboards assigned with less effective value (90%) (Tsai et al., 2008/9)
  - More conservative values for low and medium specification glove boxes (98% & 99.9%)
- Consider various confounding factors when more data become available, e.g. location of measurements, types of nanoparticles



RESPIRATORY PROTECTIVE EQUIPMENT (RPE)

Control measure		Efficiency (%) Nano dataset[A]	Efficiency (%) Proposed*	Specific sources[B]
Filtering half mask (disposable)	FFP1	*˜43 - 95*	50	APFs (EN 529, 2005 from 5 countries - Finland, Denmark, Italy, Sweden, United Kingdom), OSHA 29 CFR 1910.134 (2006), NIOSH Decision Logic (2004) ANSI Z88.2 (1992) BS 4275 (1997) Shaffer & Rengasamy, 2009 Stoffenmanager-nano
	FFP2	*˜50 – 99.999*	80	
	FFP3	*˜78 – 99.9999*	90	
Filtering half mask, unpowered (elastomeric face piece)	Half mask + P2	*˜47 – 99.997*	85	
	Half mask + P3	*˜50 – 99.9999*	90	
Filtering full mask, unpowered (elastomeric face piece)	Full Mask + P2	*˜98–99.9 (n=2)*	85	
	Full mask + P3	*˜99.5–99.9998*	90	
Powered Air Purifying Respirator (PAPR)	Helmet / hood	*(>99.9999)*	85 | 90 | 98 (TH1, TH2, TH3)	

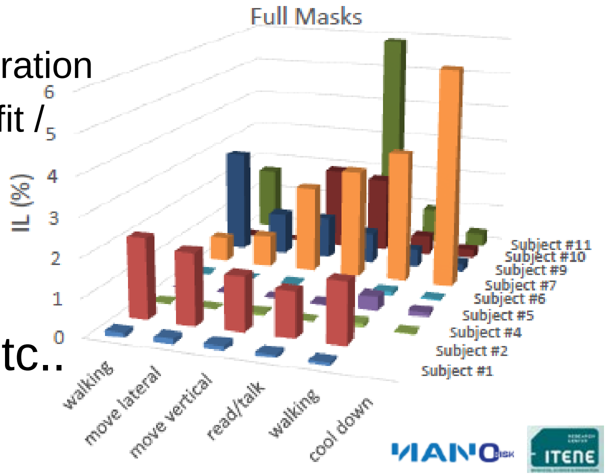
* Proposed value based on all sources
A Based on reviewed nano dataset incl. experimental data obtained in EU projects
B Specific sources that determined the proposed value

RESPIRATORY PROTECTIVE EQUIPMENT (RPE)

- Most data available on filtering (disposable) half masks under experimental conditions. No or limited data available on other respirator types

- Similar findings compared with conventional substances:
  - In some cases experimental tests show an increased efficiency of respirators for nanoparticles compared to their certified protection values
  - Total inward leakage (TIL) is by seal leakage rather than filter penetration
    - conservative values and worst case simulations (non-optimal fit / simulated leaks) were also considered to propose values

- Available data difficult to interpret considering different test types (static/dynamic), test conditions, leakage/fit, etc..



PROTECTIVE CLOTHING

Control measure		Efficiency (%)		
		Nano dataset[A]	Proposed*	Specific sources[B]
Woven materials	Laboratory (cotton) coat	*˜40 – 64*	**40 (s) | 25 (l)**	Park et al., 2011 Rengasamy et al., 2010
Non-woven materials	Polypropylene, frocks (Cat I, Type 6)	*˜70 – 99*	**70 (s) | 50 (l)**	Gao et al., 2010
	Protective clothing (e.g. Tyvek, Cat III, Types 3B, 4B, 5B & 6B; Tychem, Types 5B and 6B)	*˜92 – 99.9*	**95 (Type 3, liquid-tight) 90 (Type 4, spray tight) 90 (Type 5, particle) 85 (Type 6, lim. spray tight)**	TNsGs 2007, 2010; OECD, 2009 Gao et al., 2010 Spaan et al., 2013 Ling et al, 2012
	Protective clothing (double-side PVD coated Nylon, Cat III Type 4)	*40*	***(40)***	-
	Self-ventilated / overpressure suit (Cat III, Type 1)	*99.999 – 99.9999*	**99.9 (s/l)**	-

* Proposed value based on all sources
A Based on reviewed nano dataset, incl. experimental data obtained in EU projects
B Specific sources that determined the proposed value

GLOVES

Control measure		Efficiency (%) Nano dataset[A]	Proposed*	Specific sources[B]
Disposable protective gloves	Nitrile Thin	˜41 – 99.96	70 (s/l)	Vinches et al, 2014; Dolez et al., 2013
	Nitrile Thick	˜48 – 99.99	95 (new double gloves) 90 (s) 85 (l)	TNsGs 2002, 200; OECD, 2009 Dolez et al. (2013) Vinches et al (2014) Spaan et al., 2013
	Vinyl	-		
	Non powder Vinyl	-		
	Non powder Latex	˜77 –99.99		
Reusable	Neoprene / Natural Latex	˜77 –99.99		
	PVC	˜68 – 97		
	Butyl	˜49 – 99.99	70 (s/l)	Vinches et al, 2014 ; Dolez et al., 2013; Delpivo et al., 2016

* Proposed value based on all sources (if correct selection/guidance applies)
A Based on reviewed nano dataset, incl. experimental data obtained in EU projects
B Specific sources that determined the proposed value

From Ansell Guide, 8th Ed.

PROTECTIVE CLOTHING & GLOVES

- Limited number experimental (static & dynamic) studies currently available on a limited number of clothing types & gloves
- Protection values proposed based on experimental findings and values from Technical Notes (TNsGs) for conventional substances and other sources:
  - Very high protection values measured experimentally, more conservative values proposed for protective clothing, e.g. Tyvek, Cat III, Types 3B, 4B, 5B & 6B (85-95%)
  - For thin nitrile gloves and butyl gloves, a lower protection value is proposed (70%) compared with other gloves (Vinches et al, 2014 ; Dolez et al., 2013)
- Issues of concern for evaluation purposes:
  - Different test methods & conditions (e.g. through-diffusion & filtration-based test bench studies, static manikin and dynamic subject test protocols in chambers)
  - Different types of nanomaterials (NaCl, Ag, Fe_3O_4, TiO_2, SiO_2)

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CONSTRUCTION INDUSTRY

> 500 x OEL

100 - 500 x OEL

50 - 100 x OEL

1 - 50 x OEL

Prevention factor: 90x

GUIDANCE

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Best practices effectiveness, prevention
protection measures for control of risk
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LIFE12 ENV/ES/000178
Instruction sheets
Respiratory protection equipment
TYPES
• FFR- Particulate Filtering Face piece Respirators (Filtering half mask)
• Half Mask Respirators (Filters: P1/P2/P3)
• Full Face Masks (Filters: P1/P2/P3)
• Particulate filters (Cartridges)
CERTIFICATION AND TESTING
• EN 13274-1:2001. Respiratory protective devices. Methods of test. Determination of inw
total inward leakage
• EN 13274-7:2008 Respiratory protective devices. Methods of test. Determination of pa
penetration
• EN 149 / EN 140 / EN 136 / EN 143
MAINTENANCE AND CLEANING
• Inspect respirators for cleanliness and damage before each use.
• Filtering face piece respirators can be reused by the same worker, but only if the r
properly, its shape remains unchanged, and the filter material is not physically da
• A respirator inspection must include a check of the respirator's ability to work pr
any connections; and the condition of the various parts, such as the face piece, he
hoses, and any cartridges, canisters, or filters.
• Store respirator in sealed bag in a clean, dry, non-contaminated area.
• Replace respirator and/or cartridge or filter if it is damaged, distorted, a proper
breathing becomes difficult.
• If your respirator fails an inspection or is defective, your employer must remo
either repair it or discard it.
RECOMMENDED RPE AGAINST ENMS
Half Mask Respirators (Filters: P3)
Full Face Masks (Filters: P3)
Perform a negative or positive seal check each time before entering a contaminated area.
Local Exhaustive Ventilation (LEV)
TYPES
a) Enclosing Hoods
- Laboratory Glove Box (complete enclosure)
- Down-flow room (complete enclosure)
- Horizontal/downward laminar flow booth
- Laboratory Hood (partial enclosure)
- Walk-in booths
- Paint spray booth (partial enclosure)
b) Capturing Hoods
- Movable LEV systems (extendable arms)
- HEPA Filtered down flow booth
- Fixed Capturing Hoods
- On tool extraction
c) Receiving hoods
CERTIFICATION AND TESTING
• EN 14175-4:2005. Fume cupboards. Part 4. On-site test methods
• ASHRAE 52 2007. Method of testing general ventilation air-cleaning devices for removal efficiency by
particle size.
MAINTENANCE AND CLEANING
• Maintenance Opening: The entire mechanical and electrical equipment of the ventilation system should
be accessible via a secure and suitable opening.
• A fume cupboard function display should be installed to definitely indicate the correct functioning of the
fume cupboard airflow.
• Routine checks on LEV systems must be undertaken by appropriately trained employees. The frequency
of such checks will be determined by making reference to the manufacturer's recommendations, risk
assessment findings, previous maintenance history, etc and should be recorded in the systems logbook.
• Before use: thorough visual examination to verify the LEV is in efficient working order, in good repair and
in a clean condition.
• When installing LEV, use a reputable supplier, with experience of the type of control that is needed who
can demonstrate that their system will adequately control potential contaminants.
RECOMMENDED RPE AGAINST ENMS
- Local exhaust enclosure (Glove Box)
- Ventilated Laboratory Hood (partial enclosure)
- HEPA filtered down flow booth
- Ventilated Laboratory Hood + built-in water wash
down systems (sprays)
- Movable LEV systems (extendable arms)
- Receiving hood (hot process)
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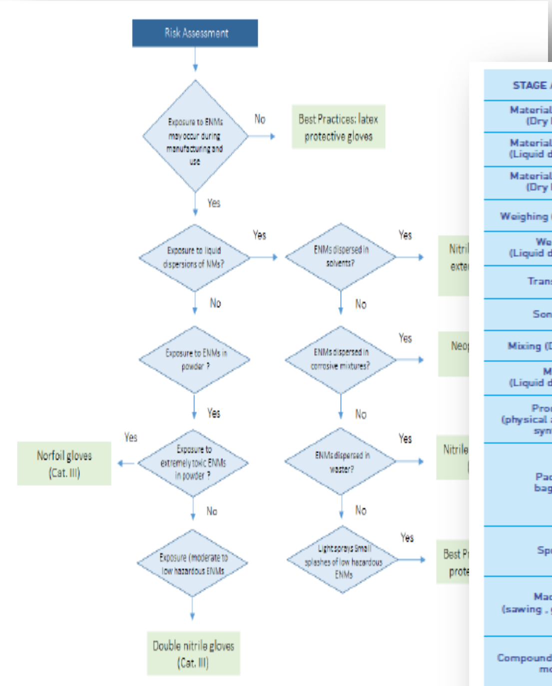
NanoRISK – Guidance on recommended measures and controls for mitigating and control the risk posed by ENMs

GUIDANCE AND RELEVANCE OF RMM IN THE WORKPLACE



STAGE / PROCESS	LABORATORY	PILOT PLANTS	INDUSTRIAL SETTINGS (MEDIUM SCALE PRODUCTION)	INDUSTRIAL SETTINGS (LARGE SCALE PRODUCTION)
Material Unpacking (Dry Powder)	Ventilated Laboratory Hood (partial enclosure) Local exhaust enclosure (Glove Box)	HEPA filtered down flow booth	Custom-fabricated enclosures HEPA filtered down flow booth	Custom-fabricated enclosures HEPA filtered down flow room
Material Unpacking (Liquid dispersions)				
Material Unpacking (Dry Powder)	Ventilated Laboratory Hood (partial enclosure)			
Weighing (Dry Powder)	Ventilated Laboratory Hood (partial enclosure) Local exhaust enclosure (Glove Box) Biological safety cabinet			
Weighing (Liquid dispersions)				
Transferring				
Sonicating	Ventilated Laboratory Hood (partial enclosure)			
Mixing (Dry Powder)	Ventilated Laboratory Hood (partial enclosure) Local exhaust enclosure (Glove Box)			
Mixing (Liquid dispersions)				
Production (physical and chemical synthesis)	Ventilated Laboratory Hood (partial enclosure)			
Packing / bag filling	Ventilated Laboratory Hood (partial enclosure)			
Spraying	Ventilated Laboratory Hood + built-in water wash down systems			
Machining (sawing , grinding, etc)	Ventilated Laboratory Hood (partial enclosure) Movable LEV systems (extendable arms)			
Compounding / injection molding	Custom-fabricated Movable LEV systems			

	VENTILATED TECHNICAL MEASURES									NON VENTILATED TECHNICAL MEASURES	
	Laboratory fume hood or cupboard	Local exhaust enclosure (Glove Box)	Receiving hood (hot process)	Movable LEV systems	Walk-in hood / booth	HEPA filtered down flow booth	Ventilated collar-type exhaust hoods	HEPA filtered down flow rooms	Custom-fabricated enclosures (fully – partial)	Continuous liner product off-loading system *	Inflatable seals
Material Unpacking	X	X				X		X	X		
Weighing (Dry Powder and liquid dispersions)	X	X			X	X	X	X			
Transferring	X				X				X		
Sonicating	X								X		
Mixing (Dry Powder and liquid dispersion)	X	X		X	X			X			
Synthesis (Dry/ liquid)	X		X						X		
Packing / bag filling	X					X	X	X	X	X	X
Spraying					X	X				X	
Machining	X			X	X				X		
Compounding / injection molding			X								

Review of Risk Management Measures for nanomaterials

ARE CURRENT RMMS EFFICIENT AGAINST ENMS ?

- If engineering controls (ECs) are **well designed**, they will be effective in limiting environmental release and workplace exposure
- Existing ECs need to be **supplemented by good practices** and the use of appropriate personal protective equipment (PPE)
- A key parameter to ensure the effectiveness of respiratory protective equipment is the **face seal**
- The use of **double gloves** is recommended. **Latex / nitrile** gloves when handling nano-powders and nanoparticles in water suspension. **Butyl rubber** gloves recommended when handling ENMs dispersed in solvents.
- The use of materials made of **non-woven high density polyethylene textile** offers excellent barrier protection for sub-micron particles

CONCLUSIONS

- A challenge to propose efficiency values considering the large scope in test methods, test conditions, materials, etc.
- More nano-specific data required for all RMMs to evaluate their efficiency (e.g. to apply a 5th perc) and consider confounding factors involved
- For exposure / risk assessment
  - Converge all the available evidence
  - Apply conservative estimate including potential variability in safe use
- More data needed of (simulated) workplace conditions to also obtain more realistic data

ACKNOWLEDGEMENTS

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