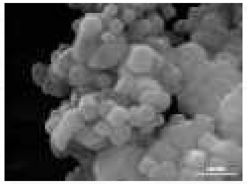
PACKAGING, TRANSPORT & LOGISTICS RESEARCH CENTER

ITENE

NanoMICEX Approach

Effectiveness of common Risk Management Measures (RMMs) to prevent and minimize exposure to ENMs in the ink & paint sector



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Join Workshop “Operational occupational Risk Management Models and tools for MNMs in the industry” / SENN Conference

SENN2015

nanoMICEX

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1. NanoMICEX approach

1. NanoMICEX approach

The activities within NanoMICEX focused on the **evaluation of the effectiveness** of relevant personal protective equipment (PPE) and engineered controls (EC) against NPs, the **definition and selection on the adequate RMMs to mitigate the risks** posed by airborne NPs, as well as the **development of safe exposure scenarios** based on the combination of safety procedures, personal protective equipment and engineering controls.

In detail, our key objectives were:

- To **evaluate the effectiveness** of the Local Exhaustive Ventilation (LEV) systems, filtration, respiratory protective equipment (RPE), skin protective equipment (SPE), and protective clothing against NPs
- To provide **scientific advice in the safe handling and use of NPs** in the workplace, including the development of safe exposure scenarios
- To define the **specifications** of common risk management measures used to protect workers dealing with nanomaterials

1. NanoMICEX approach

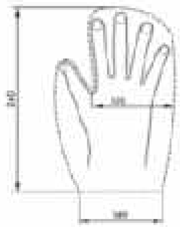
The risk management measures tested were those used commonly at industrial level, including:

- **Engineering controls**
  - Laboratory fume hoods (LEV Systems)
  - Glove boxes (LEV Systems)
- **Respiratory Protection Equipment (RPE)**
  - Disposable filtering half mask
  - Unpowered Half mask
- **Hand and body protection (SPE)**
  - Protective overalls (Laboratory coats)
  - Full Body Suit (Tyvek)
  - Chemical Splash Suit
  - Nitrile / latex gloves
- **Administrative controls**

Administrative procedures, including cleaning and maintenance operating procedures







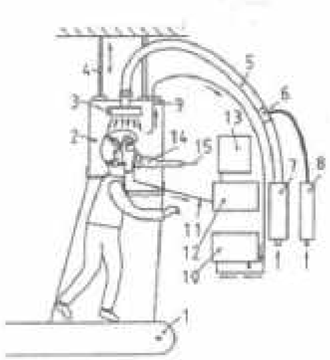
1. NanoMICEX approach

Outcomes

The main outcomes from this work were a **set of reliable data on the effectiveness of common RMMs**, recommendations to improve the performance of common **risk mitigation strategies** based on new design and/or specifications, as well as a **list of safe exposure scenarios** including a proper combination of operative conditions and RMMs. In detail, the expected outcomes are:

RMM Effectiveness

- Data on the **Penetration factor** (APF) of respiratory protection equipment (RPE)
- Reliable data on the **particle permeation / penetration potential** and for protective clothing
- Reliable data on the **barrier efficiency** for protective clothing: penetration/permeation factors
- Capture efficiency and **containment performance** of engineering controls: fume cupboards and glove boxes.
- Estimated overall reductions in exposure levels derived form the application of administrative controls




1. NanoMICEX approach

Outcomes

Proven Risk Management Strategies

- New **specifications** to be considered in the design of PPE and Engineering controls
- Integrated **strategies based on the combination of controls** and safety procedures
- Decisions trees (**tiered approach**) to select and implement adequate measures according with the exposure scenarios

Safe Exposure Scenarios

- Adequate **combinations of operative conditions (OC) and RMMs** to support the safe handling and use of target NPs in industrial settings
- Library of safe exposure scenarios based on the selection and implementation of best available controls

2. Experimental set-up

2. Experimental Sep-Up

The experimental approach applied within NanoMICEX can be split as follows:

Assessment of the effectiveness of the RMMs

This task focusses on the evaluation on the **effectiveness of RMMs to prevent or minimize exposure** in the workplace. Within this task common operative conditions are reproduced under controlled conditions to simulate the levels of exposure in the workplace.

Design and selection of RMMs

This task focusses on the **selection and definition of proven strategies** based on the outcomes of the previous tasks and information from peer reviewed publications.

Development of safe exposure scenarios

The last task focusses on the selection of adequate RMMs considering the exposure scenarios across the life cycle of the target NPs and products

2. Experimental Sep-Up

Methodology - Effectiveness Testing

1. **Design of the experimental set up**: information retrieved from the literature was studied in depth in order to clearly describe the procedures for testing according with the International Standards, including information on the following subjects:

- Specific Requirements, including the use of measurement devices, calibration requirements, sample specifications or use of radioactive sources.
- Experimental set up, including a complete description of the experimental design needed to perform the test.
- Necessary equipment: flow meters, vacuum pump, valves and other relevant devices to perform the test
- Outcomes from the test: type of information obtained with the test (e.g. permeability, retention efficiency o protection factor)
- Materials, including laboratory reagents and samples.
- Critical parameters influencing the test such as temperature, pressure, humidity, air flow, etc.

2. Experimental Sep-Up

2. **Construction of the testing equipment**: a key activity conducted within this NanoMICEX was the design and development of specific facilities to conduct the experiments.

The research team from the safety division and integrated solutions of ITENE designed Test and Research Equipment for Nanoparticles (TREN).

The first test were conducted in June 2013,where the Protection factor (APF) and leakage efficacy for three half-mask respirators were tested.

The tests were conducted using or target ENPs, being decided to use a powder aerosolizer, in this case, the Naneum powder aerosolizer PA100, which is able to generate polydisperse airborne NPs from powder samples. NaCl NPs were also tested.

Effectiveness of common RMMs to prevent and minimize exposure to ENMs

RPE (Experimental Penetration Factor)

$$PF(\%) = 100 * \left(\frac{C_{inside}}{C_{outside}}\right)$$

2. Experimental Sep-Up

3. Testing activities

- **Respiratory Protection Equipment**

- **Effectiveness testing**: the experimental penetration factor was calculated measuring the ratio between the number concentration of particles counted downstream the protective device (C_{inside})and the concentration in the testing box ($C_{outside}$)

Upstream concentrations

- CPC System 3007 – TSI (10 nm < Dp < 1 µm)
- Philips Nanotracer (Dp < 300 nm)
- Optical Particle Sizer (OPS-TSI) (0.3 µm < Dp < 10 µm)

Downstream concentrations

- CPC System 3007 – TSI
- Polycarbonate filters + SEM/TEM Analysis

2. Experimental Sep-Up

3. Testing activities

- **Dermal Protective Equipment (powder)**

- **Effectiveness testing**: The testing method for the textile is based on thorough diffusion method derivate from the ISO standard EN 374 and the ASTM F739-91 standard.

The experimental set-up for NPs in powder consists in a nanoparticle generation system, a **diffusion cell containing the protective media** to be tested and a CPC system (CPC model 9007-TSI) in order to count the nanoparticles upstream and downstream of the cell.

The protocol was optimized for different NPs in order to maintain the lowest possible pressure to avoid a high aggregation/agglomeration of the material.

2. Experimental Sep-Up

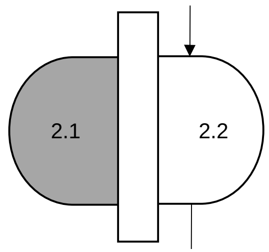
3. Testing activities

- **Dermal Protective Equipment (colloidal)**

- **Effectiveness testing**: a new test currently being validate by the ISO committees in protective clothing was applied to determine the resistance of protective gloves materials to permeation under conditions of continuous contact. The test method can be used also for protective clothing material evaluation.

  The experimental set-up for NPs consists on the measurement of the mass of the tested dispersion permeating the material per unit area per unit time (µg.cm-2min-1). It is called Breakthrough time. .

  The protocol was optimized for colloidal dispersions of NPs. The use of ICP-MS is mandatory to detect particles in the reception media (water 37 °C)



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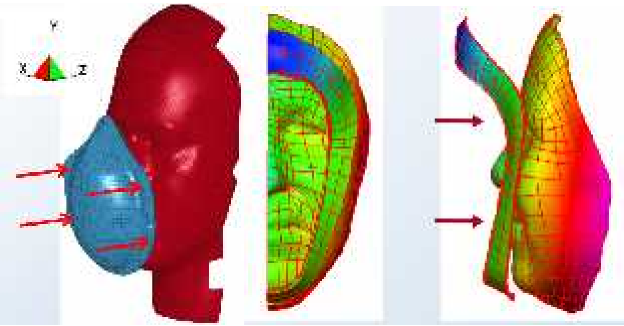
2. Experimental Sep-Up

Design of proven RMMs

Effective Personal Protective Equipment (PPE) / EC

The definition of improvements was based on the analysis of the results from the test conducted, and a through Literature review. Special attention for the following parameters:

- Degree of protection / performance level
- Usability
- Wearability / Comfort
- Aesthetics
- Durability
- Cost
- Maintainability
- Manufacturability



2. Experimental Sep-Up

Definition of Safe Exposure Scenarios

- Compilation of data form peer-reviewed journals and international publications in relation to the main parameters determining the exposure to NPs.
- Analysis of the applicability of the exposure scenario formats recommended by ECHA to support a smoother transfer/exchange of information on the safe handling and use of NPs up-and down the supply chain and across industries.
- Selection of adequate safe by design approaches, PPE and EC for each NPs and process
- Development of safe exposure scenarios based on the integration of selected RMMs and strategies and the experience and expertise of the partners involved in the project.

3. Main Results

Effectiveness of common RMMs to prevent and minimize exposure to ENMs

3. Main Results

Respiratory Protective Equipment

- Disposable and Half Mask Respirators provided **medium performance levels of filtration efficiency against nanoparticles**. Total inward leakage (TIL) ratios determined in relevant studies suggest that **face seal leakage**, and not filter penetration, is a key parameter to be considered when working with nanoparticles.

- The studies conducted within **NanoMICEX revealed significant differences in the penetration factor for similar models**. It shall be noted also that the PF characterized were in some cases higher than the recommended 5%, which means that improvements are needed to ensure a high level of protection.

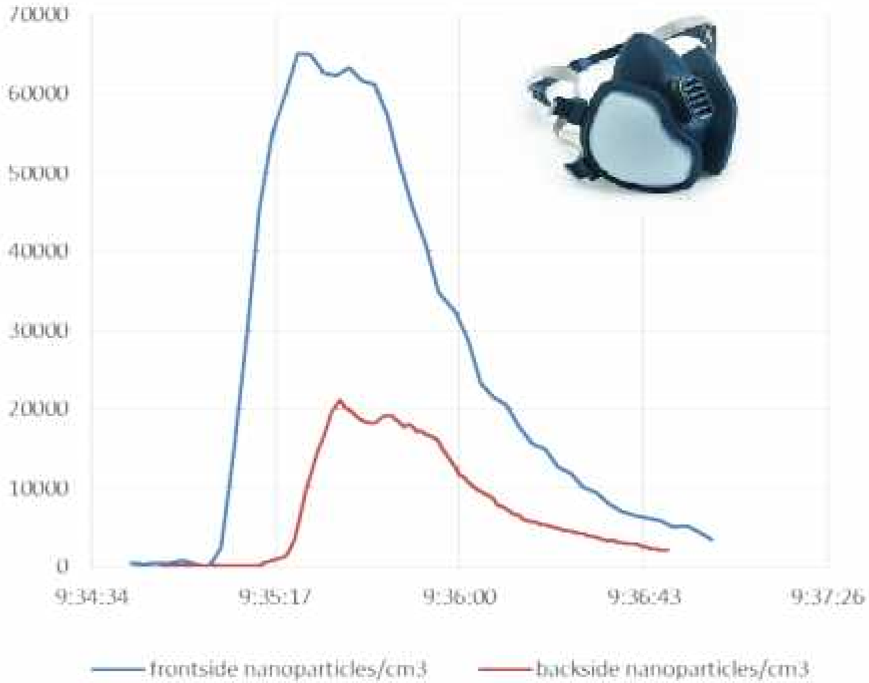
ENPs	PPE	Average Outside	Average inside	PF_{Av} %
ZnO	Aut. Mask	15125	1119,25	7,40
ZnO	HM 1	9387	797,895	8,50
ZnO	HM2	17236	2068,32	12,00
Fe_2O_3	Aut. Mask	62716	3464,43184	5,52
Fe_2O_3	HM 1	93508	6152,8264	6,58
Fe_2O_3	HM2	57783	4939,23306	8,55
TiO_2	Aut. Mask	9786	610,1571	6,24
TiO_2	HM 1	20118	1182,73722	5,88
TiO_2	HM2	48368	3149,72416	6,51
Al_2O_3	Aut. Mask	20929	1360,385	6,50
Al_2O_3	HM 1	6019	601,2981	9,99
Al_2O_3	HM2	62696	3923,95455	6,26
$CoAl_2O_3$	Aut. Mask	3790	295,62	7,80
$CoAl_2O_3$	HM 1	10164	727,289899	7,16
$CoAl_2O_3$	HM2	2100	165,165	7,87

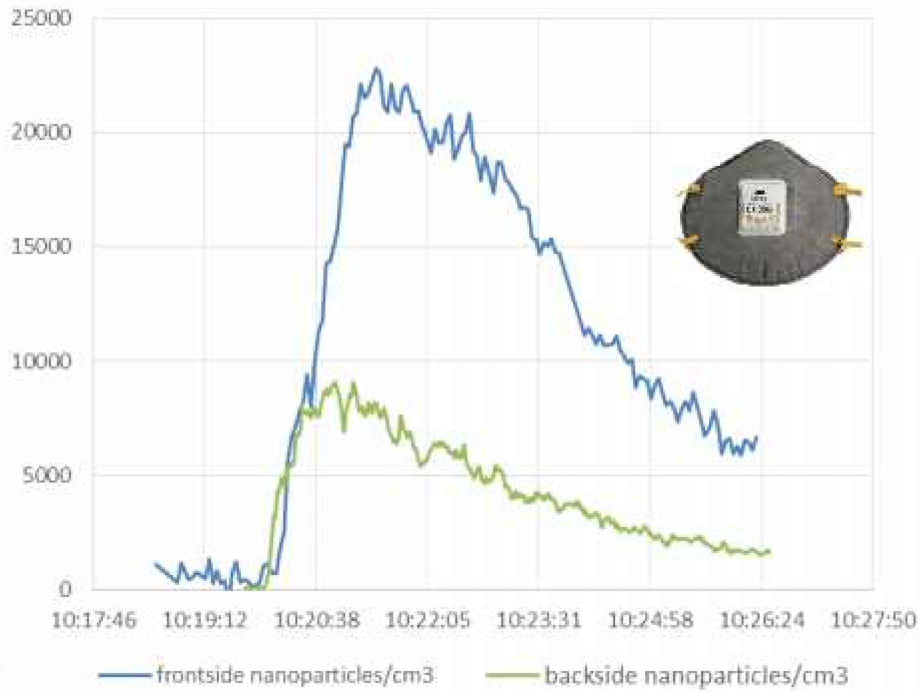
PF = 5 - 8 %

Effectiveness of common RMMs to prevent and minimize exposure to ENMs

3. Main Results

Respiratory Protective Equipment



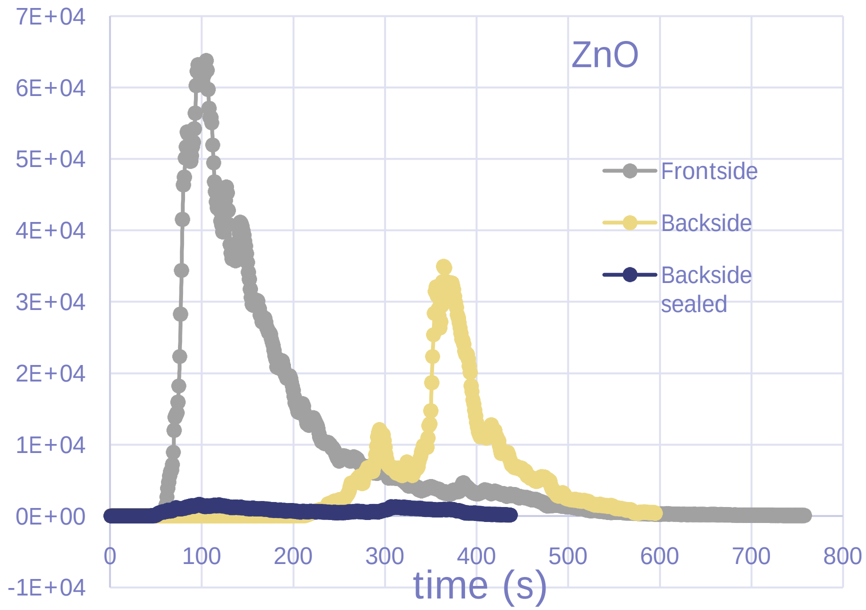


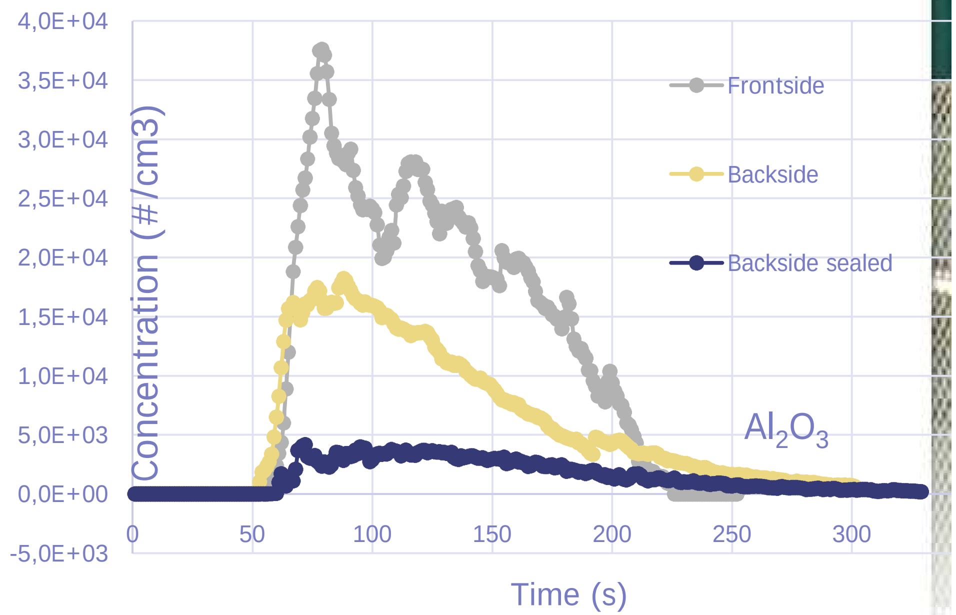
Better performance of Half Mask Respirators

Effectiveness of common RMMs to prevent and minimize exposure to ENMs

3. Main Results

Respiratory Protective Equipment





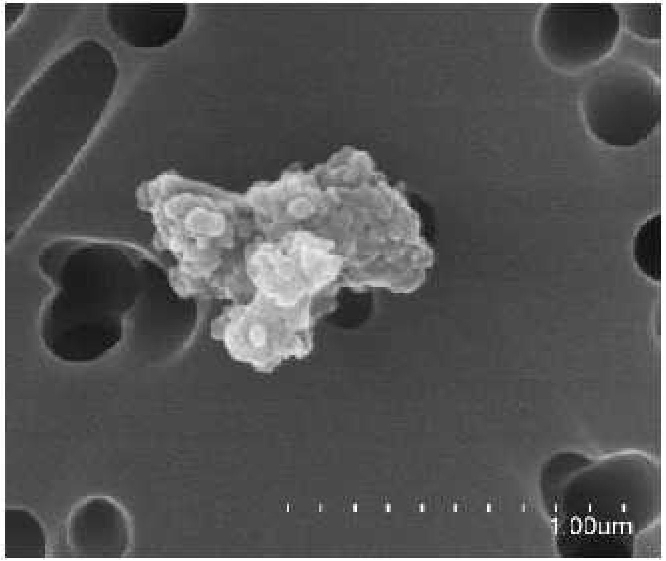
Penetration factor < 10 %

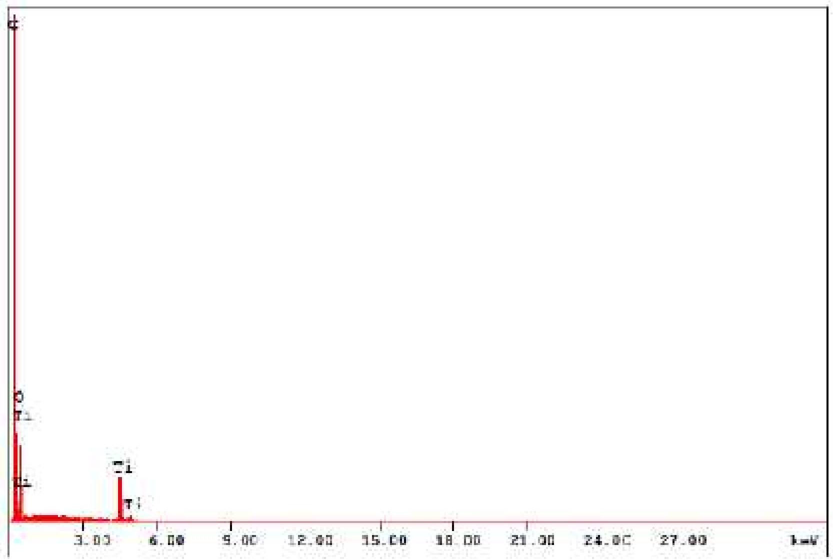
Penetration factor < 15 %

3. Main Results

Respiratory Protective Equipment

- The type and nature of ENPs measured inside the protection devices were studied collecting air samples into **polycarbonate filters for off-line physicochemical characterization** using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDXS).





3. Main Results

RPE Effectiveness - Designs

1. Recommended use of **RPE equipped with highly charged microfibers**. Much of the PPE manufacturers have available in their product catalogue half mask and full-face respirators incorporing electret media.

2. A key parameter to ensure the effectiveness of respiratory protective equipment is the face seal. It is highly recommended to use **RPE offering innovation in face seal**, ranging from new silicone based materials to inflatable seals.

   Moreover, the use of a double flange facepiece is thought to be both more comfortable and to fit better, because it didn't slip and because the second flange offered a backup seal in case of leakage through the first flange.

3. Main Results

RPE Effectiveness - Designs

3. Strap attachment and design can play an important role in the effectiveness of respirators.
4. The incorporation of an **adhesive sealing material in the face seal has also been reported to increase the fitting factor** and reduce the total inward leakage.

3. Main Results

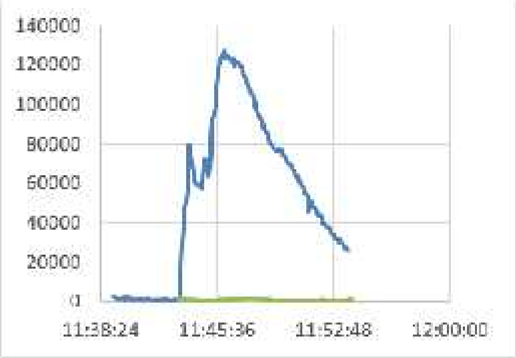
- **DPE Effectiveness:** the penetration factors were very low, meaning that gloves, suits and coats are effective against the tested ENPs. The studies conducted revealed that NPs in powder do not pass through the materials tested materials without the application of mechanical stress. In contrast, for NPs in colloidal solution, the possibility of penetration through gloves have been demonstrated.

ENPs	PPE	Max outside	Max inside	Average Outside	Average inside	PF_{plc} %	PF_{Av} %
Fe_2O_3	Latex	5177096	3566	4570527	8110	0,07±0,06	0,04±0,06
Fe_2O_3	Nitrile	3976074	1269	3610914	7258	0,03±0,07	0,03±0,07
Fe_2O_3	Lab coat	3542055	111733	3486160	77173	3,2±0,5	2,0±0,5
ZnO	Latex	1309729	0	1134595	5714	0,00±0,11	0,00±0,09
ZnO	Nitrile	2388699	226	1997458	6169	0,01±0,10	0,00±0,1
ZnO	Lab coat	4675408	111373	4140543	37599	2,38±0,19	0,8±0,2
Al_2O_3	Latex	2371340	8295	2023241	7011	0,35±0,16	0,35±0,19
Al_2O_3	Nitrile	459805	5519	435284	5103	1,2±0,2	1,2±0,8
Al_2O_3	Lab coat	1031380	102190	683621	33806	9,9±0,9	5,0±1,4
TiO_2	Latex	2147734	810	1876907	679	0,04±0,03	0,04±0,03
TiO_2	Nitrile	127236	198	122514	45	0,2±0,5	0,0±0,4
TiO_2	Lab coat	215386	23821	210896	17982	11,1±1,9	8,5±1,9
$CoAl_2O_4$	Latex	261691	1100	226487	1004	0,0±0,4	0,0±0,4
$CoAl_2O_4$	Nitrile	298351	988	251792	909	0,0±0,4	0,0±0,4
$CoAl_2O_4$	Lab coat	333363	56720	224039	33042	15±2	12±4

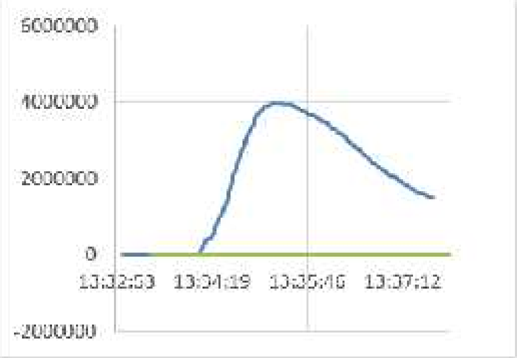
Penetration F < 5 %

3. Main Results

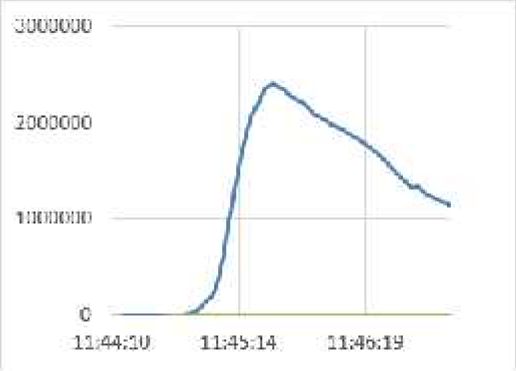
Dermal Protective Equipment



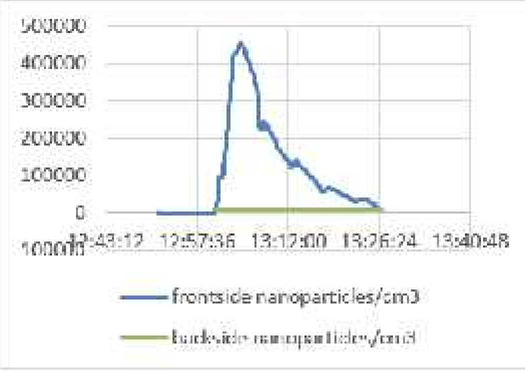
Nitrile tested with TiO_2



Nitrile tested with Fe_2O_3



Nitrile tested with ZnO



Nitrile tested with Al_2O_3

Penetration F < 5 %

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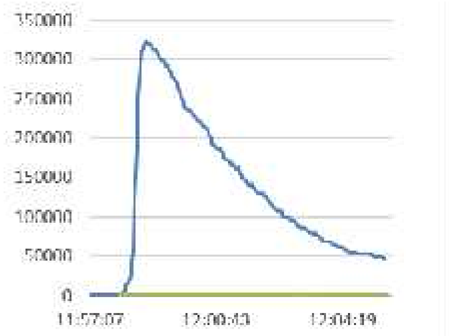
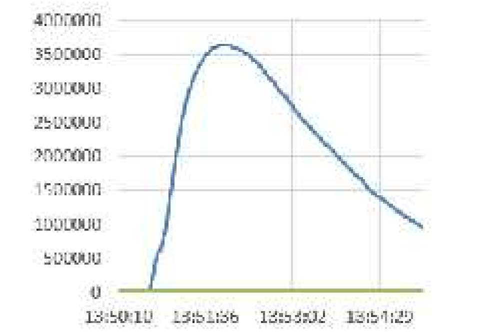
SEVENTH FRAMEWORK PROGRAMME

3. Main Results

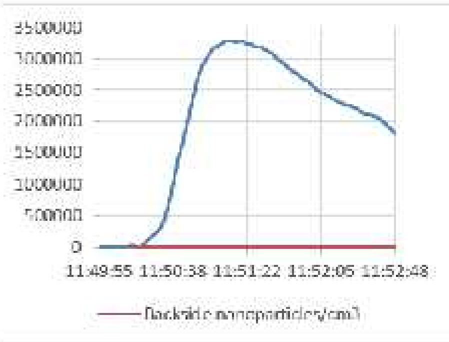
Dermal Protective Equipment



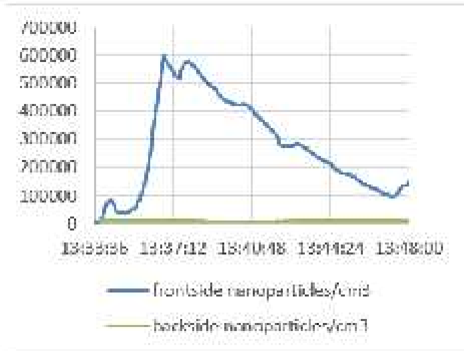
Garment tested with TiO_2



Garment tested with Fe_2O_3



Garment tested with ZnO



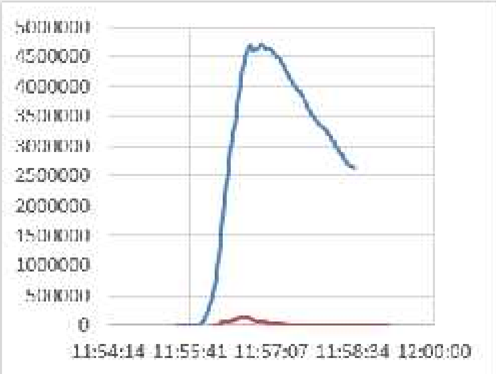
Garment tested with Al_2O_3

Penetration F < 2 %

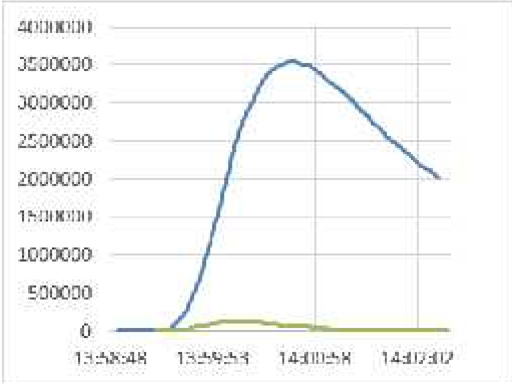
Effectiveness of common RMMs to prevent and minimize exposure to ENMs

3. Main Results

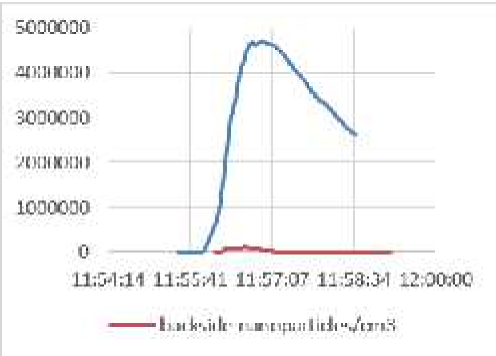
Dermal Protective Equipment



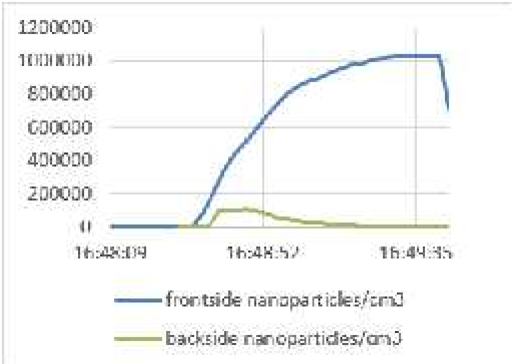
Lab coat tested with TiO_2



Lab coat tested with Fe_2O_3



Lab coat tested with ZnO



Lab coat tested with Al_2O_3

Penetration F < 5 %

3. Main Results

DPE Effectiveness - Chemical Protective Glove Designs

1. The mechanical deformations suffered by gloves in service as well as the presence of a microclimate inside the gloves may also affect the penetration of the nanoparticles. To cope with this situation, the **thickness of glove material and the requirement for textured or non-slip surfaces to improve grip** must be considered.

2. Wear **latex or nitrile gloves when handling nanoparticle powders and nanoparticles in water suspension** (glove changes should be performed frequently).

3. Great care must be taken when selecting protective gloves for handling nanoparticles in solutions. The use **of butyl rubber gloves** in highly recommended, providing excellent chemical resistance to a wide range of chemicals, including colloidal dispersions of nanoparticles.

3. Main Results

DPE Effectiveness - Protective Clothing Designs

1. The use **of non-woven materials made of non-woven high density polyethylene textile** (Tyvek ® is highly recommended. Tyvek ® offers excellent barrier protection for sub-micron particles, with up to 99% holdout of < 0.5 micron particles.

2. Avoid the use of protective clothing made with cotton fabrics. **Woven protective clothing materials offer poorer protection** than membrane materials. Additional protection against chemicals may be necessary under certain circumstances.

3. Breathability of material is another important factor to be considered. To achieve an effective protection, **protective clothing materials that can provide a combination of high barrier performance and thermal comfort** is essential.

3. Main Results

❑ LEV Effectiveness

- **Laboratory hoods and containment systems:** the measurements conducted at the researcher's breathing zone under different situations and movements (low, middle, high) reported a low quantity of NPs released . The Containment factor (Cf), the ratio of calculated concentration of the traced NP in the work space of the fume cupboard to the measured concentration in the inner part where very high in all the cases studies.

Operation	NP conc inside	NP conc bz	% Reduction
Fume hood cleaning	3,619	955	> 70 %
Opening bag	6,667	1,714	> 75 %
Transferring particles from beaker to beaker.	4,350	981	> 75 %
Mixing	5,358	1,150	> 80 %
Mean	4,998	1,200	75 %

3. Main Results

Safe Exposure Scenarios

- From the activities conducted within the project it can be stated that the development of exposure scenarios for nanomaterials continue to be a key tool for the communication of reliable measures to control the environmental, health and safety risk posed by the use of nanomaterials in occupational settings.

- Strong efforts have been done to generate libraries of ES containing information on the levels of exposure in the workplace, however, most of the information needed is often not described.

- The strategies recommended are based on the use of proven surface modifiers and proven risk management controls, including RPE, DPE and ventilation / filtration systems.

Weighing	***Administrative controls*** • Information, instruction & training; • Minimise the quantity of particulate nanomaterial in use at any one time. ***PPE*** • Safety goggles • Laboratory coat • Half-mask respirator with P3 particulate filter • Chemically resistant gloves
Mixing	***Administrative controls*** • Information, instruction & training; • Good housekeeping: containment of spills and keeping the workplace surface clean. ***PPE*** • Safety goggles • Laboratory coat • Disposable respirator with P2/ P3 particulate filter • Chemically resistant gloves
Cleaning	***Administrative controls*** • Information, instruction & training; • Good housekeeping: containment of spills and keeping the workplace surface clean. ***Engineering controls*** • LEV, preferably receiving hoods. ***PPE*** • Safety goggles • Laboratory coat • Disposable respirator or Half-mask respirator with P3 particulate filter • Chemically resistant gloves

4. Overall conclusions

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Effectiveness of common RMMs to prevent and minimize exposure to ENMs

SEVENTH FRAMEWORK PROGRAMME

4. Overall Conclusions

- As can be derived from the data presented, the control of exposure via **inhalation is a key priority for ENPs**. The tested ENPs were able to cross the respirators tested and reach the tracheobronchial area of the Sheffield head, where the real time measurement devices where located.

- The **permeation potential** is the most relevant parameter to be considered when handling nanoparticles in water/solvent dispersion. The penetration of free nanoparticles has been demonstrated to be unlikely due to the characteristics and specifications of the dermal protective equipment analyzed.

- Experimental results obtained within NanoMICEX indicate a possible penetration of nanoparticles through gloves following **mechanical deformations**. This is especially worrying in the case of occupational settings where large periods of use and contact are expected such as the case of bagging operations.

Effectiveness of common RMMs to prevent and minimize exposure to ENMs

4. Overall Conclusions

- The studies conducted to date show that the **protective measures commonly taken against dusts are also effective** against ultrafine particles and nanoparticles

- The implementation of the measures recommended within this deliverable together with good hygiene practices and proper training will ensure an **adequate level of protection** to the human health and the environment.

Exposure Route	NPs form	Type of PPE
Inhalatory	Airborne NPs	Half/full mask using highly charged microfibers as particulate material filters Double flange facepiece + adjustable straps
	Colloidal dispersion	FFP2 or FFP3 Respirators with and without valve
Dermal (Hand)	Airborne NPs	latex or nitrile glove
	Colloidal dispersion	Butyl rubber gloves
Dermal (Body)	Airborne NPs	Non-woven high density polyethylene textile (Tyvek ® type).
	Colloidal dispersion	Coated Tyvek

4. Overall Conclusions

Acknowledgments: The NanoMICEX Team

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¡THANK YOU FOR YOUR ATTENTION!

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