Scaffold Public Documents – SPD27

Innovative strategies, methods and tools for occupational risks management of manufactured nanomaterials (MNMs) in the construction industry

HIGH SENSITIVE TEST PROCEDURE FOR TESTING THE EFFICIENCY OF PERSONAL DERMAL PROTECTION EQUIPMENT AGAINST NANO-HYDROSOLS

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1. EXECUTIVE SUMMARY

This report concerns the characterization of Personal dermal Protective Equipment's (PPE) efficiency toward nanoparticles exposition via liquid phase (nanohydrosol). We try to develop generic methods for measuring the penetration of nanohydrosols through PPE materials: gloves and non-woven protective clothing. The methods developed will take into account the mechanical stresses that they undergo during their use. With these experiments, the efficiency of series of polymers and textiles against penetration of nanoparticles in suspension has been studied.

This study aims to develop generic methods for measuring the penetration of nanoparticles (NPs) to qualify the barrier effect of PPEs in liquid medium. We chose to test ultra-sensitive procedures using marked and luminescent radioactive NPs to measure the efficiency of PPEs. Radioactive isotopes have been widely used for tracing applications in diverse and varied fields such as the chemical industry [1], oil industry [2], electronics [3] or for health and environmental [4] problems. This tracing method is very sensitive and allows great flexibility of use with less analysis constraints compared to conventional chemical methods [5, 6]. Indeed it does not require special preparation step prior to analysis and it is a non-destructive method. A quantitative real-time monitoring can thus be carried out quickly. The radioisotope Eu (152) was added in the silica NPs during the synthesis; these marked NPs were used to test the efficiency of different materials of gloves which are currently used during the handling of solutions. The most frequently used are based on acrylonitrile and vinyl latex powder-free. Tyvek materials made of non-woven polyethylene or polypropylene were also chosen for this study because they are widely used in the construction sector when spraying sol-gel in a wall.

In this study, the efficiency of gloves and Tyvek against the penetration of nanoparticles in suspension containing 15nm and 40nm with continuous mechanical stress for a period of 7 hours has been demonstrated. It was proven that these PPEs were efficient and that no NPs passed through gloves and Tyvek. They seems to be a very good barrier against the passage of nanoparticles in solution.

2. OBJECTIVE

The aim of the deliverable D4.8 is to test the efficiency of different PPEs using an ultra-sensitive method based on marked and luminescent radioactive NPs. More specifically, two objectives were identified:

• Set up conception for exposing porous samples (textiles) and non-porous (polymer membranes) to NPs in liquid medium while subjecting them to mechanical stress;

• Study of the efficiency of a range of textiles and polymers used in PPEs (gloves and tyvek) towards the penetration of NPs in hydrosols during a mechanical stress.

• Evaluate the Low Limit Detection (LLD) of an ultra-sensitive method using marked and luminescent radioactive NPs and compare with a well-known method that is the ICPMS.

3. RESULTS and DISCUSSION

The efficiency of different materials constituting gloves and tyvek for protection against the different suspensions of nanoparticles was evaluated. Tyvek composed of non-woven polyethylene or polypropylene were tested because they were used in the construction sector especially for spraying mortar. Different glove materials that were frequently used during the preparation and the applying of mortars were also tested: the most commonly used are based on acrylonitrile and latex. To lower the limit detection and because SiO_2 was difficult to analyse (HF dissolution to be analysed by ICPMS and many parts of the characterization devices contained silica which can interfered with the results), the SiO2 NPs were marked with a radioactive isotope of Europium Eu 152. The radioactive tracer was fully representative of the species studied, it was not affected by these physico-chemical conditions and the detection can be done in a non-destructive manner and through a continuous wall.

✓ Synthesis of Europium marked nanoparticles:
Silica beads of 15 and 40-50 nm of size, containing radioactive Eu complexes, were synthesized according to the following synthesis method:

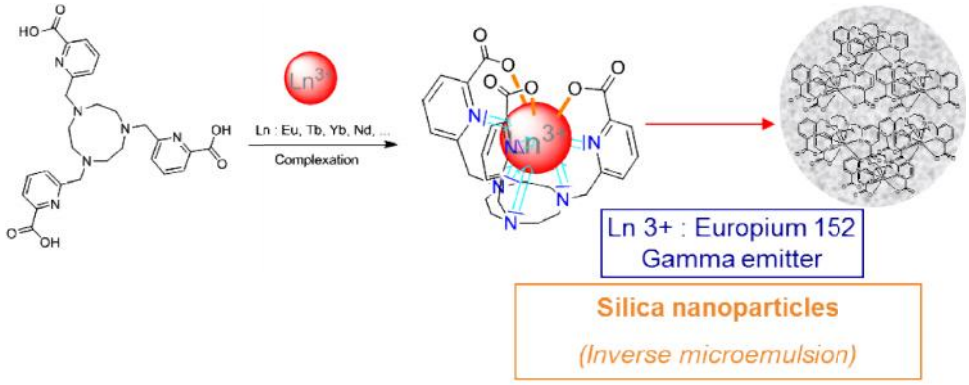

Figure 1: Synthesis of SiO_2 nanoparticles containing complex rare earth.

The stable lanthanide complexe Eu(tpatcn) was incorporated into silica nanoparticles by the reverse microemulsion process using two different surfactant systems (e.g., Triton X-100 and Igepal CO-520) to control the size of the nanoparticles. The first system was a microemulsion consisting of a quaternary mixture for synthesizing TX-100/Hexanol/Cyclohexane/Eau silica nanoparticles with a size of about 40 nm [7, 8]. The second studied system allowed to obtain smaller particles of about 15 nm, with a ternary equilibrium Igepal CO-520/Cyclohexane/Eau [8]. The final particles were dispersed in water and their morphology was characterized by TEM. For this, a drop of

the colloidal solution was deposited on the copper grid covered with a carbon film and the water was evaporated in the air. The incorporation of the organolanthanides was based on the replacement of 480µL of the previous aqueous micellar phase systems by 400µL of water and 80µL of an aqueous solution of the complex at a concentration of 0.01M. The both sizes of silica particles without and with Europium are observed on Figure 2.

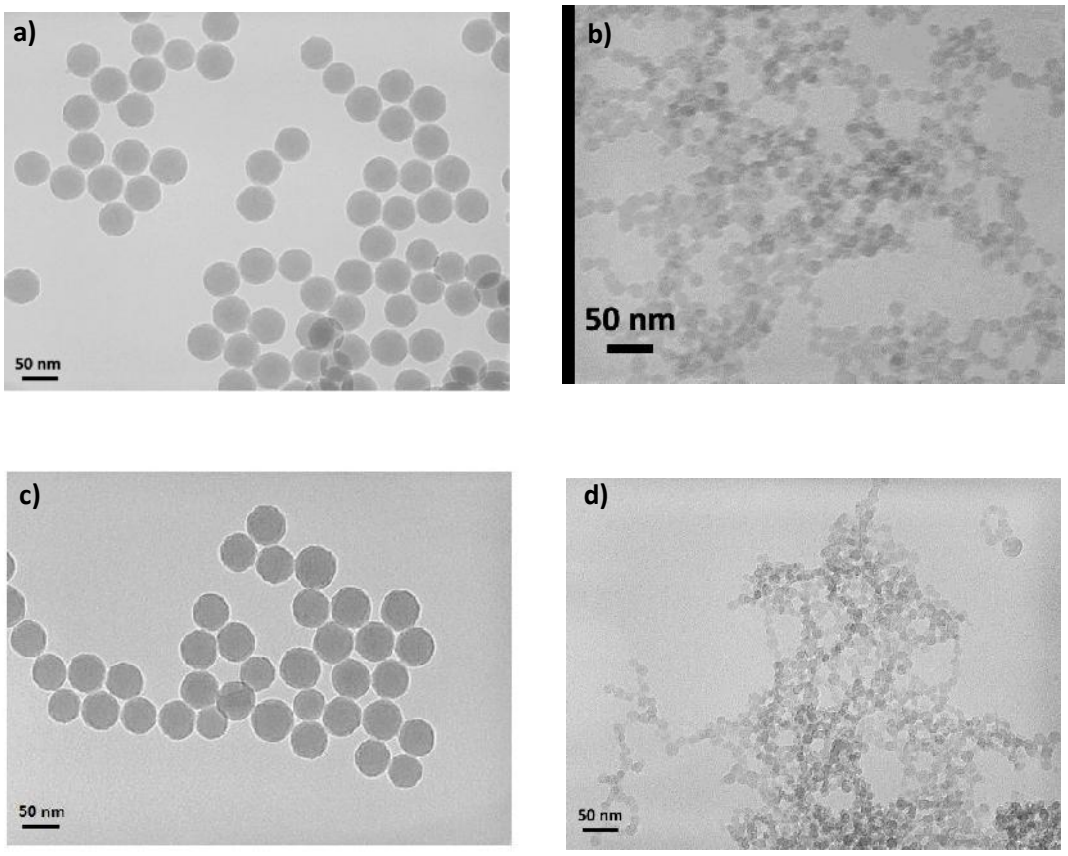

Figure 2: TEM images of silica nanoparticles obtained a) from the quaternary microemulsion (50-40nm), b) from the ternary emulsion (15nm), c) from the quaternary microemulsion (50-40nm) with [Eu (tpatcn)] and d) from the ternary microemulsion (15nm) with [Eu (tpatcn)].

The study of the stability and the efficiency of these radioactive Europium lanthanide chelate based Silica nanoparticles was published in European Journal of Inorganic Chemistry [9].

✓ Experimental set-up:

A device for measuring the distribution of the nanoparticles in the liquid phase through samples (textiles and polymers) has been developed. Devices of this type have

already been used for the diffusion test of NPs in hydrosols through PPEs or clothes. This kind of cells are generally very efficient for the determination of diffusion coefficients for low diffusive materials (Figure 3).

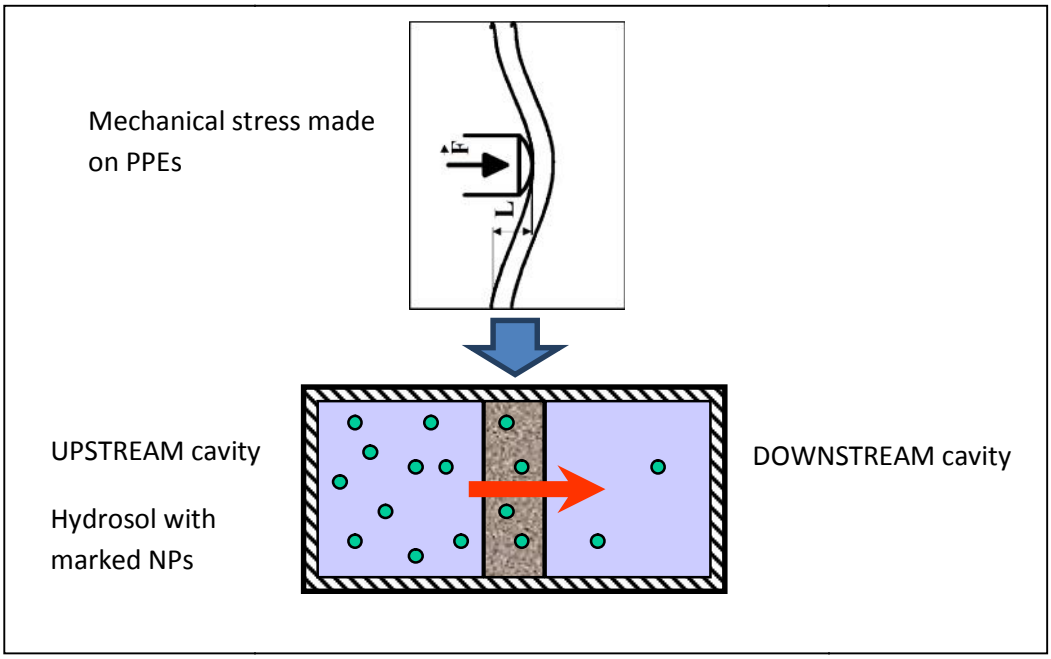

Figure 3: Diffusion cell used for the NPs trace study that can pass through the protective gloves and Tyvek and schematic drawing of the mechanical stress that PPEs undergo.

The homogenized liquid containing a known concentration of particles was introduced into the upstream cavity. The concentration of particles having diffused through the sample was measured in the downstream cavity. The diffusion coefficient of the particles in the material can then be calculated. An assembly incorporating a mechanical stress was designed. A downstream piston cavity that was used to simulate the deformation of a glove in a dynamic mode was added. The piston came and went thanks to a motor; the speed and the displacement path were adjustable (Figure 4).

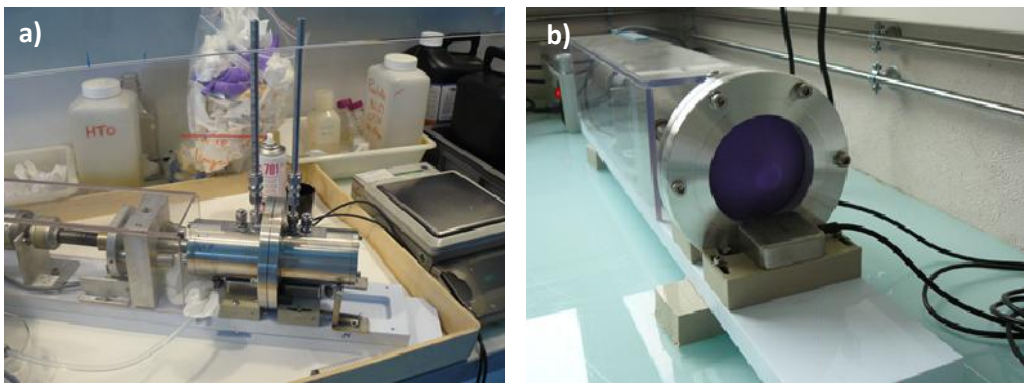

Figure 4: a) diffusion cell used in a dynamic mode with a piston and b) glove deformed by the piston.

✓ Results:

Diffusion experiments were performed in dynamic mode for 7 hours for the both types of gloves used most often, namely latex and nitrile and also for the Tyvek with the both sizes of SiO_2 NPs marked Europium (40-50nm and 15nm). At first, two solutions of SiO_2 ^{152}Eu were made with water, one for the 50nm NPs size and the other for the 15nm NPs size in order to have a γ activity of about 336 CPM/mL (Count Per Minute). The upstream and downstream parts were filled with ultrapure water, we took 6mL of water in each part and we put 6 mL of the prepared solutions in the upstream part and 6mL of ultrapure water in the same time in the downstream part to equilibrate the volumes. This manipulation was the beginning of the diffusion kinetic (T0). We took 1mL of solution in the both parts (upstream and downstream) at the same time every hour. The downstream cavity was supplemented by the volume of water corresponding to what has been taken after each collection. All the results were summarized in tables 1, 2, 3, 4, 5 and 6. The dynamic mode for the Tyvek consisted of a piston penetration of about 1cm in the Tyvek, the static mode was also investigated concerning the Tyvek. The gamma activity of the samples analyzed was determined with a gamma counter 1480 Wizard. Each analysis was performed in a 20 mL tube.

SiO_2-^{152}Eu 40nm NPs	Latex	
Dynamic mode	CPM	CPMdownstream/CPM*upstream (%)*
downstream t0	-2,2	-0,02
downstream t1h	-3,9	-0,05
downstream t2h	-5,6	-0,08
downstream t3h	-0,2	0,00
downstream t4h	0,9	0,01
downstream t5h	-2,4	-0,03
downstream t6h	1,2	0,02
downstream t7h	0,6	0,00
Upstream t0	14607,5	

Table 1: γ activity measured with a gamma counter for samples taken in the upstream and downstream cavities at different times of the diffusion experiment of SiO_2 NPs of 40 nm containing complex ^{152}Eu for latex gloves in a dynamic mode.

SiO_2-^{152}Eu 40nm NPs	Nitrile	
Dynamic mode	CPM	CPMdownstream/CPM*upstream (%)*
downstream t0	9,9	0,10
downstream t1h	6,9	0,14
downstream t2h	-0,6	-0,01
downstream t3h	3,9	0,08
downstream t5h	-2,5	-0,05
downstream t6h	-2,3	0,05
downstream t7h	13,1	0,26
Upstream t0	10175,7	

Table 2: γ activity measured with a gamma counter for samples taken in the upstream and downstream cavities at different times of the diffusion experiment of SiO_2 NPs of 40 nm containing complex ^{152}Eu for nitrile gloves in a dynamic mode.

SiO_2-^{152}Eu 15nm NPs	Latex	
Dynamic mode	CPM	CPMdownstream/CPM*upstream (%)*
downstream t0	13,7	0,33
downstream t1h	-1,7	-0,08
downstream t2h	-4,2	-0,20
downstream t3h	-3,8	0,18
downstream t4h	-0,4	-0,02
downstream t6h	0,6	0,03
downstream t7h	-0,2	0,00
Upstream t0	4141,5	

Table 3: γ activity measured with a gamma counter for samples taken in the upstream and downstream cavities at different times of the diffusion experiment of SiO_2 NPs of 15 nm containing complex ^{152}Eu for latex gloves in a dynamic mode.

SiO_2-^{152}Eu 15nm NPs	Nitrile	
Dynamic mode	CPM	CPMdownstream/CPM*upstream (%)*
downstream t0	21,7	0,38
downstream t1h	7,7	0,27
downstream t2h	4,7	0,16
downstream t3h	5,0	0,17
downstream t4h	22,9	0,80
downstream t6h	2,2	0,08
downstream t7h	1,8	0,03

Upstream t0	5737,9	

Table 4: γ activity measured with a gamma counter for samples taken in the upstream and downstream cavities at different times of the diffusion experiment of SiO_2 NPs of 15 nm containing complex ^{152}Eu for nitrile gloves in a dynamic mode.

SiO_2-^{152}Eu 15nm NPs	Tyvek	
Dynamic mode (piston 1cm)	CPM	CPMdownstream/CPM*upstream (%)*
downstream t0	12,6	1,00
downstream t1h	15,4	2,5
downstream t2h	14	2,3
downstream t4h	13,2	2,2
downstream t5h	12,2	2,0
downstream t6h	8,6	1,4
downstream t7h	43,4	3,6
Upstream t0	1209,5	

Table 5: γ activity measured with a gamma counter for samples taken in the upstream and downstream cavities at different times of the diffusion experiment of SiO_2 NPs of 15 nm containing complex ^{152}Eu for Tyvek in a dynamic mode (piston penetration of about 1cm).

SiO_2-^{152}Eu 15nm NPs	Tyvek	
Static mode	CPM	CPMdownstream/CPM*upstream (%)*
downstream t0	30,0	3,2
downstream t1h	25,7	2,7
downstream t2h	23,0	2,4
downstream t4h	19,7	2,1
downstream t5h	23,4	2,5
downstream t6h	26,4	2,7
downstream t7h	21,5	2,3
downstream t24h	26,6	2,8
downstream t96h	40,9	4,3
Upstream t0	946,5	

Table 6: γ activity measured with a gamma counter for samples taken in the upstream and downstream cavities at different times of the diffusion experiment of SiO_2 NPs of 15 nm containing complex ^{152}Eu for Tyvek in a static mode.

All the results obtained were summarized in the following Table:

Material	Type of NPs	NPs size (nm)	Type of experiment	Time of test	Analysis	Results
Latex glove	SiO_2 + 152Eu	50	Dynamic	7h	γ counting	no diffusion
Nitrile glove	SiO_2 + 152Eu	50	Dynamic	7h	γ counting	no diffusion
Latex glove	SiO_2 + 152Eu	15	Dynamic	7h	γ counting	no diffusion
Nitrile glove	SiO_2 + 152Eu	15	Dynamic	7h	γ counting	no diffusion
Tyvek	SiO_2 + 152Eu	15	Static	96h	γ counting	no diffusion
Tyvek	SiO_2 + 152Eu	15	Piston 1cm	7h	γ counting	no diffusion

Table 6: Summary of experimental conditions and of obtained results.

With all of the diffusion experiments made, we conclude that no γ activity was detected in the downstream cavity either for gloves or for Tyvek. We observed that during the experiments with 40-50nm and 15 nm size of SiO_2-^{152}Eu NPs, the downstream cavity γ activity was equal to zero and didn't change. The results were slightly different concerning the Tyvek. A little γ activity was detected but didn't change during the kinetic. It could be due to a bad cleaning of the diffusion cell and that's why γ activity was detected from the beginning of the experiment.

4. CONCLUSION

A diffusion cell has been designed for exposing porous and non-porous PPEs samples to nanoparticles in solution, while subjecting them to mechanical stresses. Detection methods with low limit of detection have been developed to quantify the possible diffusion of nanoparticles contained in hydrosol through the PPE. The use of marked NPs technique for the study of PPEs efficiency was particularly reliable and reproducible on all series tested. It helped to define precisely the percentage of NPs that can diffuse through PPEs. Unlike ICPMS, this method requires no sample preparation, which can be long and induce inaccuracies.

With this study, the efficiency of gloves and Tyvek against the penetration of nanoparticles in suspension containing 15nm and 40nm with continuous mechanical stress for a period of 7 hours has been demonstrated. It was proven that these PPEs were efficient and that no NPs passed through gloves and Tyvek.

However, this technique is uncommon in laboratories and difficult to implement in contrast to the ICPMS. When comparing the Low Limit Detection (LLD) of the both techniques, we observed that the LLD of the gamma counter for a solution containing 40-50nm SiO_2-^{152}EU NPs was not better than the LLD of the ICPMS used. We calculated that the LLD of the marked ^{152}Eu NPs was of about **$6.8\ 10^{10}$ particles/mL** whereas those of the ICPMS for SiO_2 NPs was of about **$1.67\ 10^{10}$ particles/mL**. In conclusion, ICPMS remains a good technique to quantify NPs in hydrosols because its calculated LLD was in the same range than those calculated for the gamma counter. Moreover, ICPMS is a well-known and safe quantification analysis compared to technique that uses radioactive NPs. We recommend using ICPMS for the quantification of NPs.

5. LIST OF FIGURES

6. LIST OF TABLES

7. REFERENCES

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8. APPENDIX

Calcul of DLL:

1) Gamma counter:
LLD fixed at 3 count/min by the γ counter manufacturer for Europium
Solution prepared with SiO_2-^{152}Eu beads of 40-50nm (radius of about 20nm) of size which had a γ activity of 321 000 count/min.
Concentration of the solution = 1.5mg/mL
Density of particles = 1.95 10^6g/m^3
Volume particle Vp=4/3 * π * R^3 = 4/3 * π * $(20.10^{-9})^3$ in m^3
Density = m_p/V_p and m_p = Density * V_p
M_p = 1.95 10^6 * 4/3 * π * $(20\ 10^{-9})^3$ en g
M_p = 2.04 10^{-19} g
Mole number N = concentration/m_p
N = 1.5 10-3 g/mL / 2.04 10-19g = 7.35 10^{15} particles/mL for a solution at 321 000 c/min
LLD at 3c/m corresponds to 6.8 10^{10} particles/mL
LLD ¥ counter for Europium NPs = 6.8 10^{10} particles/mL

2) ICPMS:
LLD given by the manufacturer for SiO_2 particles = 3.4 ppb = 3.4 µg/L of SiO_2 = 3.4ng/mL of SiO_2
M_p = 2.04 10^{-19} g
LDD = 3.4 10^{-9}/2.04 10^{-19} = 1.67 10^{10} particles/mL
LDD ICPMS = 1.67 10^{10} particles/mL