Experimental evaluation of individual protection devices against different types of nanoaerosols: graphite, TiO$_2$ and Pt

Luana Golanski, Arnaud Guiot and François Tardif
CEA-Grenoble, Liten, Laboratory of Tracer Technologies, France
E-mail: luana.golanski@cea.fr

Abstract. In this study different conventional individual protection devices, well-qualified for submicron particles were tested for different types of polydispersed nanoaerosols of TiO$_2$, Pt and graphite ranging from 10 to 75 nm (electrical mobility diameter). For that purpose two specific test benches were used: one for the filter-based devices which are tested under a controlled air flow and the other one for protective clothing and gloves under diffusion and without air flow.

1. Introduction
Nano-sized particles are defined as objects in the size range 1-100 nanometers (reference ISO: TS 229 QG1 PG1 and ISO TS 27687, to be published in 2008). Toxicological studies have shown that some nanoparticles can potentially have an effect on human health [1]. Manufactured nanomaterials show unique properties due to their small size and therefore present a great potential for industrial applications. The number of workers exposed to the nanoparticles may increase in the future. It is today necessary to apply the principle of precaution by implementing among other, efficient personal protections against the engineered nanoparticles in order to maintain the exposure as low as possible. The chemical, physical properties of engineered nanoparticles vary widely thus, how nanoparticles in interaction with the device may behave, even under exactly the same test conditions, could be different.

Penetration of nanoparticles into the human body may occur essentially through respiration rather than by ingestion and dermal contact. Aerosol filtering is the common way to remove particles from air. Different filter types are intensively used in a variety of domains such as nuclear, microelectronics, etc. For uncharged fibrous filter media the Maximum Penetrating Particle Size (MPPS) is between 150 and 300 nm. According to the single fiber filtration theory for fibrous filter, particles smaller than 100 nm are trapped on the filter fibers essentially thanks to random displacements due to the Brownian motion. The particles are then in general irrevocably captured by van der Waals forces. The collection efficiency of nanosize particles through fibrous filter depends on the filter characteristics, the face velocity and on the aerosol intrinsic characteristics like particle density, particle diameter [2, 3]. Experimental works performed on the penetration of different types of nanoparticles such as silver, NaCl and DOP through fibrous filter media confirmed the expected behaviour [4-6].

Electrostatic filters are constituted of fibers electrically charged during the fabrication process by Corona or triboelectric effect. These filters show a high efficiency and a low pressure drop and are therefore used for respirator masks. For electrostatic filters exposed to neutral particles, the Maximum Penetrating Particle Size (MPPS) is expected from calculations between 50 and 60 nm [2]. The shift of
the MPPS toward smaller particles for an electrostatic filter as compared to an uncharged filter is due to the effect of the fiber charge on the particle. Neutral particles passing through the media made of charged fibers are polarized by the electric field and charges are induced on the particles. Consequently, the capture of the particle is also influenced by the polarization force exercised by the fiber on the particle. Experiences performed on N95 electrostatic filters using NaCl monodispersed aerosol reported a MPPS value around 40 nm [7]. On FFP3 electrostatic filters using graphite polydisperse aerosol, the MPPS was observed to be around 30 nm [8].

In order to prevent from dermal exposure, the efficiency of protective cloths and gloves to nanoparticles penetration have to be evaluated as well. Only few works describe the influence of nanoparticle penetration through protective clothing. A previous work on protective clothing performance with regard to NaCl particle penetration has been performed in the size range of 10 to 1000 nm [8]. The results indicate that woven fabrics behave almost the same as fibrous filters with a MPPS between 100 and 500 nm.

The aim of this study was to evaluate the influence of aerosol type on the protection efficiency of commercial protective devices. In this work the efficiency of commercial protective equipments was evaluated with different types of nanoaerosols: graphite, TiO$_2$ and Pt. One commercial HEPA (High Efficiency Particle Air) filter and one electrostatic filter media were tested. The efficiency of three commercial protective clothing (made with woven and non-woven fabrics) was evaluated. The efficiency of three commercial gloves made of different materials (nitrile, latex, neoprene) and of various thicknesses was evaluated as well.

2. Materials and methods

2.1. Test benches
Two specific test benches were used in order to test the efficiency of personal protection devices against nanoparticles. The filter media is here tested with a controlled air flow containing a polydisperse aerosol. As shown by Japuntich et al. [4], the results are similar to the one obtained by the slower method using monodispersed challenge particles. The experimental set-up consists of a nanoparticle generation system, a filter support containing the filter media and a downstream pump. A detailed description of the experimental set-up is described elsewhere [8]. In this work a filter support is designed using two identical aerosol flow lines made of stainless steel: one containing the filter and the other without filter [6]. A valve allows to switch the nanoaerosol flow between the two measurement lines. The upstream and downstream particles are classified by a Differential Mobility Analyzer (DMA model 5.5-300, Grimm) and then measured by a Condensation Particle Counter (CPC model 5.403, Grimm). The filtration penetration is calculated as 1-(downstream concentration / upstream concentration).

The through diffusion bench was designed in order to reproduce the actual conditions of use of clothing (without an important air flow). The experimental set-up consists in a nanoparticle generation system, a diffusion cell containing the protective media to be tested and a CPC system (CPC model 5.403, Grimm) in order to count the nanoparticles in the down stream part of the cell. A detailed description of the experimental set-up is described elsewhere [8]. In the upper stream part of the cell, a continuous flow of graphite, TiO$_2$ and Pt nanoparticles is injected in order to maintain a constant concentration of nanoparticles. The differential pressure between the two parts of the cell is maintained at a few mbars in order to test the media efficiency without imposing any flow. In the down cell, the CPC takes samples of initially filtered air containing the nanoparticles which have diffused through the media. The number of particles flowing per minute in the down stream part of the cell was measured in order to estimate the efficiency of the protective clothing. For all the measurements a $^{85}$Kr radioactive source is used in order to neutralize the nanoaerosol before introducing into the test filter or the diffusion cell.

Graphite nanoparticles are generated by spark discharge between two graphite electrodes. TiO$_2$ and Pt nanoparticles are produced by a glowing wire: the material is evaporated by passing a high current
through a conducting wire, suspended in a flowing gas. The mean geometric diameter was typically about 35 nm for graphite aerosol. Smaller particles with size centered 10 nm are obtained only using the glow wire generator. The maximum mean diameter obtained by glowing wire generator was 40 nm for TiO\textsubscript{2} nanoparticles.

2.2. Materials
The efficiencies of a HEPA and an electrostatic commercial filter were evaluated when exposed to Pt and TiO\textsubscript{2} aerosols. The filters characteristics used in this study are given in the following Table 1.

| Fiber material | HEPA | Electrostatic filter |
|----------------|------|----------------------|
| Thickness (mm) | 0.33 | -                    |
| Weight (g/m\textsuperscript{2}) | 75±5 | -                    |
| 0.3 \(\mu\)m DOP Penetration (at 5.3 cm/s) | < 0.3\% | < 1\% |
| Solidity | 0.064 | - |
| Class given by the manufacturer | H11 according EN 1822 | FPP3 according EN 149 |

Different types of protective clothing (thicknesses and materials) as listed in Table 2. They were tested using through diffusion method with Pt, TiO\textsubscript{2} and graphite nanoaerosols. The efficiency of cotton, polyester (used for protective clothing in clean room) and high density polyethylene materials was investigated.

Table 2. Specifications of the protective clothing media tested by through diffusion technique.

| Name  | Thickness (\(\mu\)m) | Type     | Material                        |
|-------|-----------------------|----------|---------------------------------|
| Media 1 | 650                  | Woven    | Cotton                          |
| Media 2 | 115                  | Non-woven| High-density Polyethylene textile Tyvek® |
| Media 3 | 160                  | Woven    | Polyester                       |

The efficiency of commercial gloves made of different materials and thicknesses as listed in Table 3.

Table 3. Specifications of gloves tested by through diffusion method.

| Name | Thickness (\(\mu\)m) | Material |
|------|-----------------------|----------|
| Glove 1 | 100                | Nitrile  |
| Glove 2 | 150                | Latex    |
| Glove 3 | 700                | Neoprene |

3. Results and discussion

3.1. HEPA filters
The efficiency of an HEPA glass fibrous filter was evaluated for particle diameters ranging between 9 and 19 nm at a flow speed \(v = 5.3\) cm/s for different types of nanoaerosols: Pt, TiO\textsubscript{2} and graphite (Figure 1). Tests were performed with graphite nanoparticles centered around 35 nm. For TiO\textsubscript{2} and Pt the mean diameter is around 10 nm.

The filter shows higher efficiency for graphite nanoaerosols than for TiO\textsubscript{2} and Pt for particles ranging between 10 and 20 nm. A difference up to more than one order of magnitude is observed for a given particle diameter. TiO\textsubscript{2} nanoaerosols have the highest penetration through the filter: the maximum penetration for 19 nm particles is around 0.2\%. The penetration of TiO\textsubscript{2} and Pt through a given filter is of the same order of magnitude. The fibrous filter efficiencies for graphite, TiO\textsubscript{2} and Pt nanoaerosols increase with decreasing the particle size as predicted by the classical filtration model thanks to Brownian diffusion [2]. However the filtration model does not take into account the influence of the aerosol type on the filtration efficiency [2].
3.2. Electrostatic filters
Further, the efficiency of an FPP3 electrostatic filter was investigated for TiO$_2$ and graphite particle diameters ranging between 15 nm and 75 nm at the flow speed $v = 5.3$ cm/s. Tests were performed with TiO$_2$ nanoparticles centered around 45 nm and for graphite particles centred around 35 nm (as shown in Figure 2).

3.3. Protective clothing
Different types of protective clothing, woven and non-woven were tested using through diffusion method with Pt and TiO$_2$ nanoaerosols.

The efficiencies of cotton, polyester (used as protective clothing in clean room) and high density polyethylene (specifications given in Table 2) were investigated. The number of particles flowing per minute in the down stream part of the cell was measured by CPC (Figure 3). The background noise of
the measurement is kept below five particles/cm$^3$. Tests were performed first with TiO$_2$ and Pt nanoparticles centered around 10 nm and with a maximum concentration ranging between $7 \times 10^5$ part/cm$^3$ and $2 \times 10^6$ part/cm$^3$. The measurements, repeated three times on the same protective clothing, are found reproducible.

![Figure 3](image-url) **Figure 3.** Evolution of clothing efficiency for TiO$_2$ and Pt nanoparticles as measured by through diffusion technique.

Cotton and protective clothing present almost the same efficiency when tested with TiO$_2$ and Pt particles centered around 10 nm. Non-woven fabrics (air-tight materials) are more efficient against Pt and TiO$_2$ nanoparticles centered around 10 nm than woven cotton and polyester. This is consistent with observations [8] made for graphite nanoparticles centered around 40 nm and 80 nm.

3.4. Gloves
Gloves made of three different materials *i.e.* nitrile, latex and neoprene (specifications given in Table 3) were tested with TiO$_2$ and Pt nanoparticles in static conditions. Gloves were exposed to graphite nanoparticles centered around 10 nm. The concentration in the up part of the diffusion cell was constant to be around $10^5$-$10^6$ particles/cm$^3$. The differential pressure between up and down parts of the cell is fixed to few mbars in order to keep a diffusion regime. The background noise of the measurement is kept below five particles/cm$^3$. The measurements, repeated three times on the same glove is found reproducible. No TiO$_2$ and Pt nanoparticles centered around 10 nm penetration through the gloves is observed. Gloves are found very efficient for TiO$_2$ and Pt nanoaerosol penetrations. No nanoparticle penetration through the gloves is observed when exposing the glove during a few minutes. Other tests are in progress aiming at creating conditions more favorable to diffusion, although not necessarily corresponding to correct glove use: stretched gloves, long exposure time, increased differential pressure.

4. Conclusions
HEPA filters show a higher efficiency for graphite nanoaerosols than for TiO$_2$ and Pt nanoaerosols: a difference up to more than one order of magnitude was observed for a given particle diameter in the range 10-20nm.

The HEPA filter efficiency for TiO$_2$ and Pt nanoparticles is in the same order of magnitude.

At MPPS around 35 nm, the electrostatic FPP3 filter is more efficient for graphite than for TiO$_2$ nanoparticles. The difference in efficiency is increases, up to one order of magnitude on each side of the MPPS.

Cotton and polyester clothings showed close efficiencies when tested with TiO$_2$ and Pt nanoparticles centered around 10 nm. Air-tight fabrics made of non woven textile seem much more efficient to protect workers against Pt, TiO$_2$ nanoparticles than cotton and polypropylene.
Gloves are found very efficient for TiO$_2$ and Pt nanoaerosols with particle centered around 10 nm. No nanoaerosol penetration through the gloves is observed.

**Acknowledgements**

These results have been obtained in the frame of FP6 European program Nanosafe 2.

**References**

[1] Oberdörster G 2000 *Phil. Trans. Roy. Soc. London Ser. A* **358** 2719
[2] Hinds W C 1999 *Aerosol Technology: Properties, Behavior, and Measurement of Airborne particles* 2nd edition Wiley-Interscience
[3] Benoit Hervé-Bazin 2007 *Les nanoparticules: un enjeu majeur pour la santé au travail* EDP Sciences ed.
[4] Japuntich D A, Franklin L M, Pui D Y, Kuehn T H, Kim S C and Viner A S 2007 *Journal of Nanoparticle Research* **9** 93
[5] Kim S C, Harrington M S and Pui D Y H 2007 *Journal of Nanoparticle Research* **9** 117
[6] Heim M, Mullins B J, Wild M, Meyer J and Kasper G 2005 *Aerosol Science and Technology* **39** 782
[7] Balazy A, Podgorski A and Gradon L 2004 *Journal of Aerosol Science* **35**(S2) 967
[8] Golanski L, Guiot A, Rouillon F, Pocachard J and Tardif F 2009 *Human and Experimental Toxicology*