

Experimental evaluation of personal protection devices against graphite nanoaerosols: fibrous filter media, masks and protective clothing

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ABSTRACT

In this study, conducted in the frame of the European Nanosafe2 project, different conventional engineering and personal control systems, well-qualified for micron particles (fibrous filters, masks and protective clothing) were tested with graphite nanoparticles ranging from 10 to 100 nm. For that purpose 2 specific test benches were constructed: one for the filter-based devices which are tested under a controlled air flow and the other one based on the "through diffusion method" derived from standard NF EN ISO 6529. This paper will describe the operational conditions and the obtained results.

Keywords: nanoparticles, filtration, fibrous filters, clothing

1. INTRODUCTION

Nano-sized particles are often defined as particles in the size range of less than 100 nanometers. Manufactured nanomaterials show unique properties due to their small size and therefore present a great potential for industrial applications. Analysts have estimated that the worldwide market for nanoparticles will be about 340 billion Euro in 2011 which would rank it alongside the automobile and microelectronic industries. Consequently the number of workers exposed to the nanoparticles may increase in the future. Potential impact of these new materials on human health was suggested [1]. Long before the final conclusions of toxicology research studies, it is today necessary to apply the principle of precaution by implementing among other, efficient personal protections against the engineered nanoparticles in order to decrease the exposure.

Penetration of nanoparticles into the human body may occur through respiration and dermal contact. Aerosol filtering is the common way to remove particles from air. Different filter types are intensively used in a variety of applications such as respiratory protection, nuclear processing, hazardous materials and clean rooms. For uncharged fibrous filter media the Maximum Penetrating Particle Size (MPPS) is measured between 150 to 300 nm. The efficiency of commercial filters is evaluated at the MPPS. According to conventional filtration theory, particles smaller than 100 nm are submitted to random displacements due to Brownian motion which enhances the collision probability with the fibers. The particles are then irreversibly captured by van der Waals forces. Nevertheless, the filtration efficiency to nanoparticles could be affected by the thermal rebound effect during filtration due to the particle bounce on the fiber filter. This phenomenon was predicted by H. C. Wang and G. Kasper

[2] through theoretical considerations. It would occur for particle sizes around 10 nm and below. However at this date, most of the experimental work performed on the penetration of different types of nanoparticles like silver, NaCl and DOP through fibrous filter media did not show any experimental evidence of the thermal rebound [3], [4], [5]. Only one of these studies performed with a liquid aerosol (DEHS) reported a thermal bounce effect for particles size as big as 20 nm [6]. Electrostatic filter media used in N-series respirator masks were already challenged with NaCl nanoparticle in order to evaluate their efficiencies [7]. These filters, presenting a low pressure drop, are constituted of fibres electrically charged during the fabrication process. In this case, charged particles are captured also by the electrostatic attraction. In order to prevent from dermal exposure, the efficiency of protective cloths has to be evaluated. A previous work on protective clothing performance with regard to NaCl particle penetration has already been performed in the size range of 10 to 1000 nm [8]. Results indicate that woven fabrics behave almost the same as fibrous filters with a MPPS comprised between 100 and 500 nm.

The main goal of this work is to quantify the efficiency of commercial protective equipments to graphite nanoparticles. The tested particles range from 10 to 100 nm. A comparison between various commercial filters HEPA (High Efficiency Particle Air), ULPA (Ultra Low Particulate Air) and an electrostatic filter media was performed. The efficiency of various protective clothing (made with woven and nonwoven fabrics) to graphite nanoparticles was evaluated as well.

2. EXPERIMENTAL METHODS

Two specific test benches were used in order to test the efficiency of personal protection devices against nanoparticles.

2.1 Filter test bench

A classical bench to test filter efficiency has been designed. The filter media is here tested with a controlled air flow containing a polydispersed aerosol. As shown by [3], the results are similar to the one obtained by the slower method consisting to use monodispersed challenge particles. The experimental set-up consists of a nanoparticle generation system, a filter support containing the filter media and a down stream pump. A Palas (model GFG 1000) particle generator is used in order to generate a polydispersed graphite aerosol in the range of 10 to 100 nm. A ⁸⁵Kr radioactive neutralizer is used to put particles at the Boltzmann equilibrium. The neutralized graphite nanoparticles are then introduced into the test filter. The particle upstream and downstream the filter are first 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 $1 - (\text{the ratio of the downstream concentration and upstream concentration})$.

2.2 Through diffusion test bench

The through diffusion bench was designed in order to reproduce the conditions of use of clothing (without an important air flow). This method is based on the "through diffusion method" derived from standard NF EN ISO 6529 and NF EN 374. The experimental set-up consists in a nanoparticle generation system, a diffusion cell containing the protective media to be tested and a CPC system in order to count the nanoparticles in the down stream part of the cell. The same Palas particle generator is used in order to generate a polydispersed graphite aerosol in the nano-sized particle range. Then a ^{85}Kr radioactive neutralizer is used. In the upper stream part of the cell, a continuous flow of graphite nanoparticles is injected in order to maintain a constant concentration of nanoparticles. The concentrations upstream of the diffusion cell is about $5 \cdot 10^6 \text{ part/cm}^3$. In the down stream part of the cell, a CPC takes samples containing the nanoparticles which have diffused through the media. The differential pressure between the two parts of the cell is rigorously maintained at zero in order to test the media efficiency without imposing a flow.

3. RESULTS

3.1 Fibrous filters

The specifications of the tested filters are given in Table 1. HEPA and ULPA filters are classified by the manufacturer according to the European Standard EN 1822. The class of the electrostatic filter is given by NF EN 149.

Name	Class	Main application
HEPA 1	-	Nuclear monitoring
HEPA 2	H12	Engineering control system
HEPA 3	H14	Idem
ULPA	U15	Idem
Electret	FPP3	Respirator masks

Table 1: Specifications of the tested filter media.

Results are showed in Figure 1. Most tests on fibrous HEPA filters are confirming the conventional filtration theory: penetration decreases monotonously when particle diameter decreases as predicted by the Brownian capture model. These results obtained with graphite nanoparticles are consistent with others described in the literature obtained with DOP, Ag, NaCl particles. Moreover no thermal bounce is observed until 10 nm. Consequently these filters are even more efficient for smaller nanoparticles than for 100 nm. Nevertheless for certain types of HEPA filters represented by HEPA 2 filter in Fig.1 the penetration does not decrease monotonously: it features a plateau from 80 nm to 20 nm in the showed example. Among all the tested filters the HEPA cellulose filter used

in nuclear monitoring, the HEPA H14 and the ULPA U15 showed the best efficiency for smaller particles.

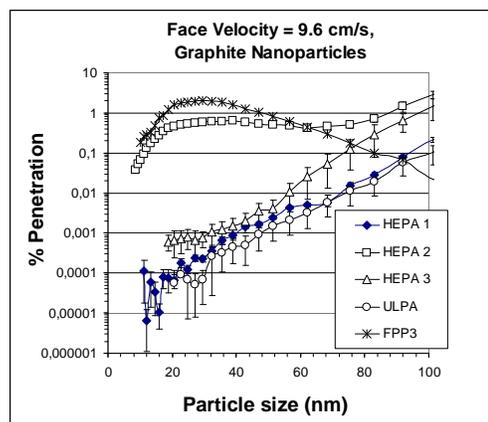


Fig.1 Evolution of graphite nanoparticle penetration for HEPA fibrous filters, ULPA fibrous filter and an electrostatic filter as a function of particle size for a face velocity of 9.6 cm/s.

3.2 Electrostatic filters

The electrostatic filter FPP3 showed a lower efficiency compared with a fiberglass HEPA filter tested at same face velocity. For electrostatic filters the MPPS was observed to be around 30 nm. This result is in accordance with a recent study [7] performed on N95 filters with NaCl monodispersed aerosol for respirators masks. The authors reported a MPPS value around 40 nm.

The filtration efficiency for the FPP3 electrostatic filter in experimental conditions closer to real use was evaluated with graphite nanoaerosol.

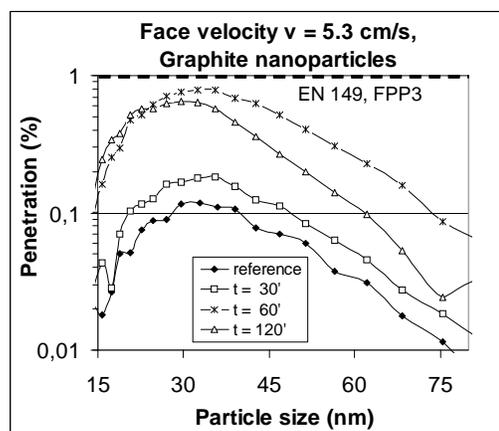


Fig.2 Evolution of graphite nanoparticles penetration through the FPP3 electrostatic filter as a function of particle size (nm) with or without moisture induced by human respiration.

The penetration of nanoparticles through the FPP3 electrostatic filter increases when used, due to the moisture bring by human respiration. For the tested masks, after 2 hours of utilization the penetration of nanoparticles through an FPP3 electrostatic filter is found just below the

maximum allowed penetration certified by NF EN 149. (defined for NaCl particles centered at 0.6 μm). It appears necessary to perform the integrity test on this kind of masks with challenge particles centered around 30 nm.

3.3 Protective clothing

The efficiency of protective clothing made of different material types, of various thicknesses were evaluated as well. Table 2 shows the characteristics of the protective clothing tested.

Name	Thickness (μm)	Type	Material
Media 1	650	Woven	Cotton
Media 2	320	Non-woven	Polypropylene
Media 3	210	Non-woven	Polyethylene textile Tyvek

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

The number of particles flowing per minute in the down stream part of the cell was measured (Fig. 3). Tests were performed with 2 graphite nanoparticle challenges centered around 40 nm and 80 nm and measured by CPC.

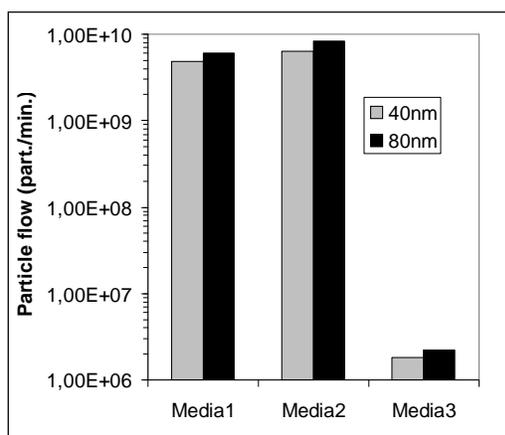


Fig.3 Evolution of clothing efficiency to graphite nanoparticles measured by through diffusion technique.

A significant difference in efficiency between different fabric media was observed. Non-woven Tyvec® clothing seems more efficient (air tight materials) against nanoparticle penetration than cotton or polypropylene. On the other hand these protective clothing are not pleasant to wear. Innovation is needed in that field.

4. CONCLUSION

The efficiency of various protective devices challenged with graphite nanoparticles from 10 to 100 nm was evaluated. For this purpose two specific test benches were constructed. HEPA fibrous filters made of cellulose and glass-fiber were both tested. As expected from the classical filtration theory the particle penetration decreases

continuously when the particle diameter decreases down the MPPS thanks to the Brownian motion capture mechanism. No evidence of thermal rebound was observed with graphite nanoparticles until 10 nm.

An increase of nanoparticle penetration through the tested FFP3 electrostatic filter was observed under the moisture bring by human respiration.

For clothing, air-tight fabrics made of non woven textile seem much more efficient to protect workers against nanoparticles than cotton and polypropylene.

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