DETERMINATION OF PERMEABILITY OF ULTRA-FINE LEAD OXIDE AEROSOLS THROUGH MILITARY FILTERS

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Abstract

Military filters introduced in the Army of the Czech Republic are most commonly used when working with combat equipment and weapons and in manoeuvring activities in the terrain with the use of explosives or chemical warfare agents. During such activities, a large number of pollutants in the form of nanoparticles are released. Nanoparticles, irrespective of their chemical composition, are classified as carcinogenic to humans and therefore it is necessary to eliminate them from the air. Military filters, especially the combined ones, which contain a filtration as well as sorption component, are most widely used and are designed for the widest range of pollutants. However, the current methodology to evaluate the effectiveness of military filters does not fix a duty to monitor the ability of the filters to capture relevant pollutants across the whole range of sizes. The paper evaluates the efficiency of selected types of military filters using the methodology and instrumentation introduced in the accredited laboratories of the Institute of Analytical Chemistry of the Academy of Sciences of the Czech Republic. The testing has been carried out simultaneously with two concentrations of ultra-fine aerosols containing lead oxide nanoparticles ranging in size from 7.6 nm to 299.6 nm. It is an aerosol, the physicochemical and toxicological properties of which are known. During the work the basic parameters of permeability of aerosols tested by filters have been evaluated, especially: size and number of particles in front of and behind the filter, the efficiency and penetration of nanoparticles by the filter.

Keywords: Nanoparticle, filter, efficiency, health safety

1. INTRODUCTION

Airborne particles may be dangerous to human health. Generally, these particles represent an adverse effect on the respiratory and cardiovascular system. Many of them occur in the air in the form of nanoparticles and rank among human carcinogens of Group 1 reported by the International Agency for Research on Cancer (since 2013) [1]. From the medical point of view, the influence of nanoparticles on the pulmonary system is particularly important [2].

1.1. Military environment

Ultra-fine particles (UFP, diameter less than 100 nm) are ubiquitous in the workplaces and in the urban atmosphere and pose a significant health hazard to humans. Repeated smog situations are monitored when the legal limits for airborne dust and selected chemical pollutants in the air are exceeded. Due to the expected introduction of specialized nanotechnologies in the armament of the Army of the Czech Republic (ACR), it is necessary to be engaged in the UFP monitoring process. Another reason is the fact that military nanotechnologies have their own specific features as compared with common industrial nanoproducts, which have to be taken into account when estimating their health risks. In the ACR, military explosives and chemical warfare agents, emitted into the air in the form of aerosols, rank among the most common threats [3]. This applies not only to the training of combat units, but also to the selected workplaces of military units, military repair facilities and workplaces carrying out the delaboration and ecological disposal of ammunition and explosives, where the personnel can be exposed to their irradiation.

1.2. Protective equipment

Filter respirators are respiratory protective equipment introduced in the ACR. One of their most important parts is usually a filter canister, the functional parts of which are stored in a plastic or metal housing. In accordance with the CSN EN 132 technical standard [4], the particle filter is a separate filter or is usually a part of combined filters that are capable of entrapping dispersed solid and liquid particles, and specified gases and vapours from the passing air. There are three classes of particle filters with an increasing efficiency marked from1 to 3. They are labelled with the colour code white: P1 to P3.

Most of modern filters are combined (including anti-particle and anti-gas layers) [5]. Such filters must usually comply with a number of technical standards, such as ČSN EN 143 [6], ČSN EN 12942 [7] and ČSN EN 14387 [8] in the Czech Republic. Until now, the testing of military and fire filters as a protection against the inhalation of nanoparticles from the air is not mandatory and, therefore, the effectiveness of these filters against nanoparticles has not been confirmed officially. The technical requirements for military means of individual protective equipment, military protective masks, names and definitions are set by Czech Defence Standard 841503 (COS 841503) [9].

1.3. Types of filtration

From the viewpoint of filtration mechanisms, we divide filtration into the surface and depth filtration. The principle of surface filtration is the mechanical capture of each particle, which is larger than the space between the filter fibres. On the other hand, in depth filtration, more forces are applied simultaneously - Van der Waals forces, electrostatic forces and the forces induced by surface tension. The total efficiency of capture of ultra-fine aerosols (E) [%] is a combination of all capture principles. Share of these principles in the overall efficiency varies with the size and shape of each particle, where G1 is the amount of dispersion behind the filter, G2 is the total amount of dispersion in front of the filter and the proportion G1 / G2 is the penetration (P) [10]:

$$E = \left(1 - \frac{G_1}{G_2}\right) \cdot 100 \qquad (1)$$

For calculation of the permeability coefficient (K_p) [%], the calculation stated in COS 841503 has been exploited. In COS 841503, the maximum permissible permeability coefficient of the paraffin oil aerosol in the protective filters for universal combined arms masks is set at a maximum level of 0.001 % [9]:

$$K_P = \frac{G_1}{G_2} \cdot 100 \qquad (2)$$

2. MATERIALS AND METHODS

2.1. Preparation of lead oxide (PbO) nanoparticles

PbO nanoparticles (PbONP) were generated continuously in situ in a tubular reactor in hot condition using the evaporation-oxidation-condensation technique, in which a ceramic crucible containing a small amount of lead wire was placed inside a ceramic tube of a vertically oriented furnace (Carbolite TZF 15/50/610, Carbolite Limited, UK). The molten portion of lead was vaporized at 830 °C in the centre of the furnace. The metal vapours were transferred from the furnace through an inert stream of nitrogen and diluted with an air flow; then oxygen oxidized lead to lead oxide. Both flows were set to 3 l / min with Mass Flow Controllers (MFC). The lead oxide nanoparticles were diluted in the second step with the air flow (20 l / min) and then passed through a filter firmly located in a specially developed sampling device (see **Figure 1**). During the measurement, the aerosol flow rate was set to 95 l / min.

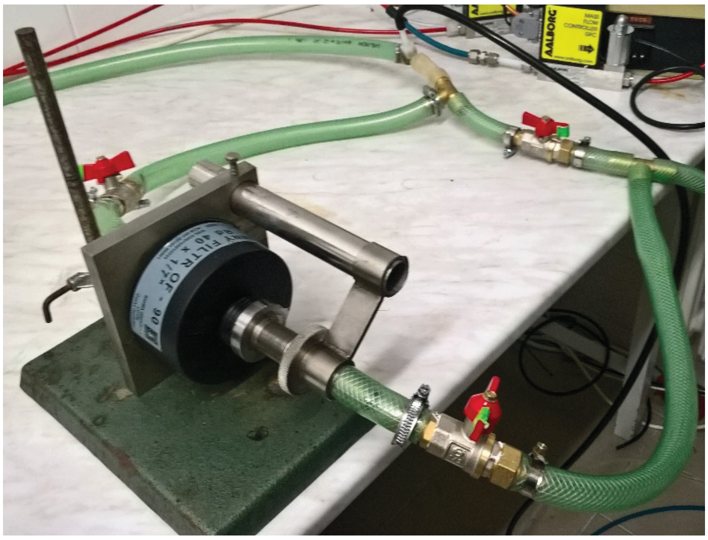


Figure 1 Sampling device (Source: own)

2.2. Characterization of generated PbO nanoparticles and tested filters

Table 1 Tested filters (Source: own)

Filter	Diameter	Height	Weight	Usage against	Maximal K_p [%]
OF-90	110 mm	90 mm	260 g	Solid and liquid substances and aerosols of poisonous substances according to CSN EN 143 class P3, biological aerosols and radioactive dusts	0.001 [9]
Filter P3	110 mm	50 mm	90 g		0,05 [6]
Filter P3 with two threads 40 × 1 / 7´´	110 mm	65 mm	130 g		0,05 [6]
Filter MOF-2	110 mm	90 mm	260 g	Chemical warfare agents in the form of gases and vapours, solid and liquid aerosols of poisonous substances according to CSN EN 143 class P3, biological aerosols and radioactive dusts	0,05 [6]
Filter MOF-4	110 mm	90 mm	260 g		0,05 [6]
FN (Nuclear ULPA filter AX6650HS)	/	/	72 $g \cdot m^{-2}$	Heavy industry environment, chemical industry, laboratories, pharmaceutical industry, remediation activities	0,05 [6]

Regarding the particle concentration, the nanoparticle distribution was measured directly using the Scanning Mobility Particle Sizer (SMPS, model 3936L72, TSI Inc., Shoreview, USA) continuously in the sizes of 7.6 - 299.6 nm [11]. The nanoparticle measurements were performed using the SMPS before and after passing through the filter at two concentrations (the total particle concentration before entering the filter was approximately 1.2×10^6 particles·cm^{-3} and 1.7×10^5 particles·cm^{-3}). The samples were measured four times at five-minute intervals (in total the tenth to twenty-fifth minute). The long-term stability of PbONP formation was high. The relative standard deviations in the mean particle diameter (i.e. 25.8 nm) and the total particle concentration (i.e. 1.2×10^6 particles·cm^{-3}) were 3.9 % and 3.1 %. These values show that both the generation of nanoparticles and the measurement of their size distribution using the SMPS were very reproducible. All tested filters and their detailed specifications are defined in **Table 1**.

3. RESULTS

The SMPS measured results with the distinction of 64 channels per decade. These results were evaluated using the Aerosol Instrument Manager software that enables exportation values for particular channels of normalized particle number concentrations in analysed sample of the air (NC_i). NC_i is given by the equation, where C_i [$N\cdot cm^{-3}$] is particle number concentration for i-th channel and D_i is the diameter of particles measured in i-th channel:

$$NC_i = \frac{C_i}{\log_{10} D_{i+1} - \log_{10} D_{i-1}} \quad (3)$$

Regarding the decadic logarithms of width of each channel are identical with the distinction of 64 channels per decade, therefore, it applies:

$$C_i = \frac{NC_i}{64} \quad (4)$$

On the basis of this equation, values of un-normalized number concentrations from values of normalized number concentrations for each channel were calculated. Furthermore, total particle number concentration (C_N) was calculated, where n means total number of channels:

$$C_N = \sum_{i=1}^{n} C_i \quad (5)$$

3.1. Measured values

The values of particle concentrations before and after the passage through a particle or combined filter were performed at two concentrations, 1.2×10^6 particles$\cdot cm^{-3}$ and 1.7×10^5 particles$\cdot cm^{-3}$. For each concentration, 4 measurements at 5-minute intervals were performed and the average particle concentration was determined. Then the concentration values were recalculated to particle penetration through the filter or, if need be, to the permeability coefficient K_p. The resulting values measured for individual filters ranging from 7.6 nm to 299.6 nm are shown in **Table 2**.

Table 2 Average permeability coefficient and efficiency of all tested filters [%] (Source: own)

Concentration		MOF-4	OF-90	MOF-2	P3	FN	P3 with two threads
1.2×10^6 particles$\cdot cm^{-3}$	K_p [%]	0.075	0.060	0.046	0.048	0.074	0.064
	E [%]	99.925	99.940	99.954	99.952	99.926	99.936
1.7×10^5 particles$\cdot cm^{-3}$	K_p [%]	0.500	0.421	0.375	0.486	0.520	0.385
	E [%]	99.500	99.579	99.625	99.514	99.480	99.615

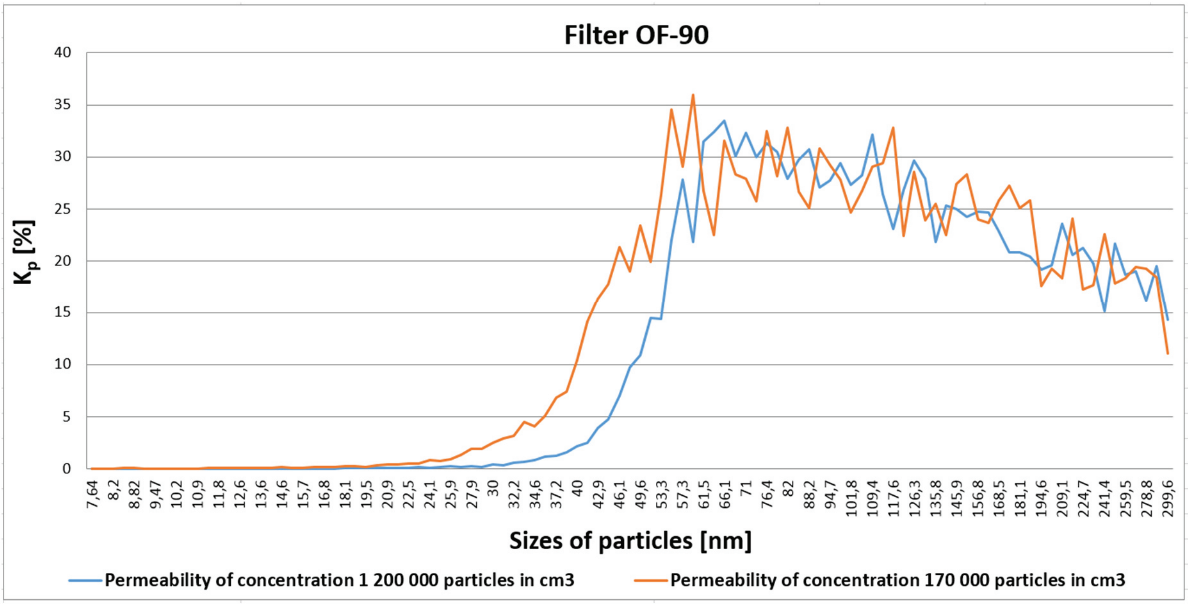
In the basic tactical and technical requirements, very high requirements were set for the permeability coefficient of MOF filters [12]. According to ČSN EN 143, the maximum permeability coefficient K_p of the test aerosol of paraffin oil and sodium chloride 0.05 % [6] is determined for P3 filters. Similarly, K_p 0.001 % is valid according to ČOS 841503 [9] for paraffin oil aerosol penetration, implemented according to CSN EN 14387 [8]. The measured K_p for individual filters exceeds this limit on an average about 60 times for a higher particle concentration and on an average about 450 times for a lower concentration. The reason is probably the modified method, when the aerosol of lead oxide is used for testing as well as the range of measurements focused on the area of ultra-fine aerosols.

3.2. Filter OF-90

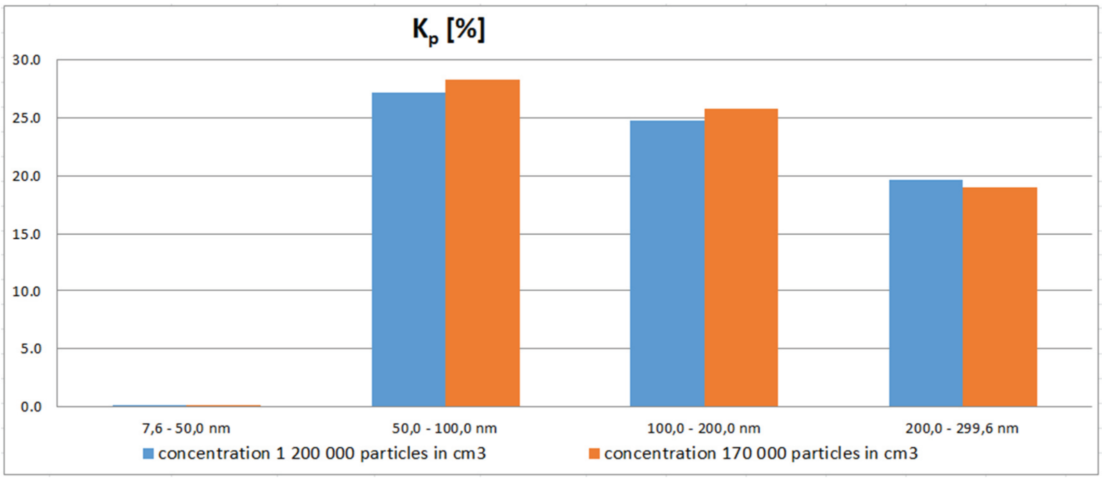
For the OF-90 combined filter, the K_p value was measured and calculated across the range of performed measurements. The highest permeability of the filter was measured for nanoparticle sizes from 50 to 100 nm. This can be documented by the values shown in **Table 3**, Graph 1 and Graph 2.

Table 3 Acquired results in different size ranges of nanoparticles for filter OF-90 (Source: own)

Concentration		7.6 – 50.0 nm	50.0 – 100.0 nm	100.0 – 200.0 nm	200.0 – 299.6 nm
1.2×10^6 particles·cm^{-3}	Kp [%]	0.024	27.223	24.801	19.692
	E [%]	99.976	72.777	75.199	80.308
1.7×10^5 particles·cm^{-3}	Kp [%]	0.164	28.340	25.830	18.979
	E [%]	99.836	71.660	74.170	81.021



Graph 1 Average permeability of particles in different sizes of particles (Source: own)



Graph 2 Permeability coefficient of PbO nanoparticles in different size ranges of nanoparticles (Source: own)

4. CONCLUSION

Within the experiment described, measuring the filtration efficiency of the antiparticle filters introduced in the ACR and in the population protection has been carried out with the use of the ultra-fine aerosol of lead oxides. The experiments have been performed in the laboratories of the Institute of Analytical Chemistry of the Czech Academy of Sciences. The measurement has been made at two concentrations performed with aerosol particle sizes in the range of 7.6 to 299.6 nm. The experiments have shown that with the use of ultra-fine aerosols of lead oxides the required maximum permeability coefficients for the test aerosol were exceeded. The reason is probably the modified method when an aerosol different from the standard one and the different measuring range aimed at the area of ultra-fine aerosols, have been used for the testing. The results of the experiment can correspond to the theory of aerosol filtration, when different proportions of surface and depth filtrations have been applied. Experiments have shown that the dimensions of the particles, which are most affected by this phenomenon, are in the range of 50 to 100 nm.

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