Determination of permeability of ultra-fine cupric oxide aerosol through military filters and protective filters

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Abstract. The paper evaluates the filtration and sorption efficiency of selected types of military combined filters and protective filters. The testing was carried out with the use of ultra-fine aerosol containing cupric oxide nanoparticles ranging in size from 7.6 nm to 299.6 nm. The measurements of nanoparticles were carried out using a scanning mobility particle sizer before and after the passage through the filter and a developed sampling device at the level of particle number concentration approximately 750000 particles·cm⁻³. The basic parameters of permeability of ultra-fine aerosol passing through the tested material were evaluated, in particular particle size, efficiency of nanoparticle capture by filter, permeability coefficient and overall filtration efficiency. Results indicate that the military filter and particle filters exhibited the highest aerosol permeability especially in the nanoparticle size range between 100–200 nm, while the MOF filters had the highest permeability in the range of 200 to 300 nm. The Filter Nuclear and the Health and Safety filter had 100% nanoparticle capture efficiency and were therefore the most effective. The obtained measurement results have shown that the filtration efficiency over the entire measured range of nanoparticles was sufficient; however, it was different for particular particle sizes.

1. Introduction
Nanomaterial is defined as a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as agglomerate and where 50% or more of the particles with one or more external dimensions are in the size range 1-100 nm [1]. Under certain circumstances, solid and liquid particles in the air adversely affect the health status of people. These are primarily aerosols made up of ultra-fine particles with a mean aerodynamic diameter in the range of several μm to nm. Such inhaled particles have a wide range of effects and most commonly damage the cardiovascular and respiratory tract [2]. The toxicity of nanoparticles has been clearly demonstrated in some biological systems, but this attribute depends largely on the size, shape, surface and reactivity of the particles. The effect may also be influenced by the susceptibility of an individual [3].

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1.1. Military environment

Ultra-fine particles (UFP) are ubiquitous in workplaces, even in urban environments and pose a significant health hazard to humans. Repeated smog situations are monitored when the legal limits of airborne dust and selected chemical pollutants in the air are exceeded. Due to the expected introduction of specialized nanotechnologies to the Army of the Czech Republic (ACR), it is necessary to be involved in the UFP monitoring process. Another reason is that military nanotechnology has its own specific features over normal industrial nanoproducts, which must be taken into account when estimating their health risks. In the ACR, the most common threats are military explosives and chemical weapons emitted into the air in the form of aerosols [4]. This applies not only to the training of combat units but also to selected departments of military units, repair workrooms and workplaces carrying out delaboration and ecological disposal of ammunition and explosives, where the staff can be exposed to their influence.

1.2. Protective military filters

Respiratory protective devices in the ACR are most often filter respirators. Filter respirator consist of a capsule filter, the functional part, which is stored in a plastic or metal housing. In accordance with the Czech technical standard 132 (CSN EN 132) [5], the particulate filter is a separate filter or is usually part of combined filters that are capable of entrapping dispersed solid and liquid particles and designated gases and vapors from the passing air. Particle filters can be of three classes, with increasing efficiency marked 1 to 3 (P1, P2, P3) and they are marked with a white color code.

Most modern filters are combined (including anti-particle and anti-gas layers) [6]. Such filters usually have to comply with a number of technical standards, such as CSN EN 143 [7], CSN EN 12942 [8], CSN EN 14387 [9] in the Czech Republic. Until now, testing of military and fire protection filters as a protection against inhalation of nanoparticles from the air is not mandatory. Therefore, the effectiveness of these filters against nanoparticles is not officially confirmed. The technical requirements for military means of individual respiratory protection, military protective masks, names and definitions are set by Czech Defense Standard 841503 (CDS 841503) [10].

1.3. Evaluation of filtration

From the point of view of the filtration mechanism, we divide filtration into a 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 fibers. On the other hand, in depth filtration, more forces are applied simultaneously - Van der Waals forces, electrostatic forces and forces induced by surface tension. Total efficiency of capture of ultrafine aerosols (E) [%] is a combination of all capture principles and their share in overall efficiency varies with the size and shape of each particle, where G1 is the amount of dispersion after the filter, G2 is the total amount of dispersion before the filter and the proportion G1 / G2 is the penetration (P) [11]:

\[ E = \left( 1 - \frac{G_1}{G_2} \right) \times 100 \]  

For calculation the permeability coefficient (Kp) [%], the calculation given in CDS 841503, where the maximum permissible paraffin oil aerosol permeability coefficient of protective filters for all army protection masks is set at a maximum of 0.001% [10] and a formula (2) is used:

\[ K_p = \frac{G_1}{G_2} \times 100 \]  

2. Materials and methods

Cupric oxide nanoparticles (CuONP) were continuously synthesized in an accredited laboratories of the Institute of Analytical Chemistry of the Czech Academy of Sciences.
2.1. Preparation of cupric oxide (CuO) nanoparticles

CuONP were synthesized by aerosol route in a flow tube reactor by thermal decomposition of the organic precursor of copper acetylacetonate (Aldrich) and subsequently oxidized in Carbolite TZF 15/50/610, Carbolite Limited, UK at 700 °C in the presence of 15.1% vol. of oxygen. Copper acetylacetonate vapours were obtained from the solid form of copper acetylacetonate in a saturation vessel at 148.2 °C. The released vapours were transported with nitrogen (flow rate 0.8 L·min⁻¹, purity 5.5) to the flow reactor. The total nitrogen/oxygen mixture flow rate was 2 L·min⁻¹. The CuONP nitrogen stream was mixed with air flow (96 L·min⁻¹) at the reactor outlet and used for both commercial and army filter experiments in a specially developed sampling device (see figure 1).

![Sampling device](source:own)

Total particle number concentrations of produced CuONP (Cₙ) after mixing with air were 4.88 x 10⁷ particles·cm⁻³ on average. The size of generated CuO nanoparticles ranged from 7.6 to 299.6 nm. The nanoparticle concentration and particle size distribution in the inhalation chamber were continuously measured by scanning mobility particle sizer (SMPS, model 3936L72, TSI, USA). The counts of nanoparticles at the input of the filter are shown in figure 2. Figure 2 below illustrates number concentrations of particular sizes of nanoparticles in measured range. The maximum amount of nanoparticles is entering the tested filters in the range of particle sizes between 30–40 nm. Samples were measured sequentially, four times at five-minute intervals (total ten to twenty-five minutes).

![Number size distribution of particles before entering filters](source:own)
2.2. Method for evaluation of acquired results

Acquired results were reviewed using Aerosol Instrument Manager software that exports data of normalized particle number concentrations in analysed sample (NC\textsubscript{i}). NC\textsubscript{i} was calculated by the equation (3):

\[
NC_i = \frac{C_i}{\lg D_i - \lg D_{i-1}}
\]

where \( C_i \) [N / cm\textsuperscript{3}] is particle number concentration for \( i \)-th channel and \( D_i \) is the diameter of particles measured in \( i \)-th channel. The decadic logarithms of widths of channels are identical with the distinction of 64 channels per decade:

\[
C_i = \frac{NC_i}{64}
\]

Total particle number concentration (\( C_N \)) was calculated by the equation, where \( n \) means total number of channels:

\[
C_N = \sum_{i=1}^{n} C_i
\]

2.3. Characterization of generated CuO nanoparticles and tested filters

With regard to particle concentration, nanoparticle distribution was measured directly by SMPS [12]. The nanoparticles were measured using SMPS before and after passing the filters at a particle number concentration before entering the filter \( (C_i) \) of about \( 7.5 \times 10^5 \) particles\cdot cm\textsuperscript{-3}.

In our measurement, the military filter OF-90, which belongs to the standard equipment of every soldier in ACR, was included. In addition, another type of protective filters may be used depending on the environment and pollutant levels in the ambient air. Such filters are usually used by the Fire Rescue Brigade (FRB), but occasionally by the ACR as well. That is why our research included a wide range of protective filters, used by the Czech FRB. All tested filters and their detailed specifications are defined in table 1.

**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 [10]            |
| Filter P3     | 110 mm   | 50 mm  | 90 g   |                                                                                  | 0.05 [7]              |
| Filter P3 with two threads 40 × 1 / 7” | 110 mm | 65 mm | 130 g |                                                                                  | 0.05 [7]              |
| 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 [7]              |
| Filter MOF-3  | 110 mm   | 90 mm  | 260 g  |                                                                                  | 0.05 [7]              |
| Filter MOF-4  | 110 mm   | 90 mm  | 260 g  |                                                                                  | 0.05 [7]              |
| Filter MOF-5  | 110 mm   | 90 mm  | 260 g  |                                                                                  | 0.05 [7]              |
Filter                  | Diameter | Height | Weight | Usage against                                                                 | Maximal $K_p$ [%] |
|-----------------------|----------|--------|--------|-------------------------------------------------------------------------------|--------------------|
| Scott Health and safety CFR 22 CBRN A2B2E1K1-P3 RD               | 40 mm    | /      | 300 g  | Gases and vapours from organic compounds with a boiling point above 65 °C, inorganic gases and vapours, e.g. chlorine, hydrogen sulphide, hydrogen cyanide, acid gases and vapours e.g. sulphur dioxide, ammonia and organic ammonia derivatives (EN 14387), other gases and vapours tested: chloropicrin, cyanogen chloride, sarin, hydrogen cyanide, mustard gas and phosgene as well as CS and CN, Arsine, DMMP, particulates: solid and liquid toxic and radioactive particles and microorganisms, e.g. bacteria and viruses | 0.05 [7]           |
| FN (Nuclear ULPA filter AX6650HS)                               | /        | /      | 72 g·m⁻² | Heavy industry environment, chemical industry, laboratories, pharmaceutical industry, remediation activities | 0.05 [7]           |

### 3. Results

Particle number concentrations ($C_i$) measured before and after passage through a particulate or combined filter were performed at initial concentration of an aerosol of 7.5 $\times$ $10^5$ particles cm⁻³.

#### 3.1. Measured values

Four measurements were made at 5 minute intervals (at 10, 15, 20 and 25 minute) and the average particle concentration was determined. Concentration values were then recalculated to particle penetration by the filter, respectively the permeability coefficient $K_p$. The resulting values measured for individual filters ranged from 7.6 nm to 299.6 nm. Acquired results are shown in table 2 and figure 3.

**Table 2** Average permeability and efficiency of all tested filters [%] (source:own).

|                | $E$ [%] | $K_p$ [%] |
|----------------|---------|-----------|
| FN             | 100.000 | 0.000     |
| P3 with two threads | 100.000 | 9.561·10⁻⁵ |
| P3             | 100.000 | 7.136·10⁻⁵ |
| MOF-2          | 99.999  | 7.028·10⁻⁴ |
| MOF-3          | 100.000 | 3.576·10⁻⁶ |
| MOF-4          | 100.000 | 7.517·10⁻⁶ |
| MOF-5          | 100.000 | 5.063·10⁻⁵ |
| Scott Health and safety OF-90 | 100.000 | 3.671·10⁻⁶ |
In past years, very high tactical and technical requirements have been set for the coefficient of permeability of the MOF protection filters [13]. According to CSN EN 143, the maximum permeability coefficient $K_p$ of the test aerosol of paraffin oil and sodium chloride 0.05% [7] is determined. Similarly to military filters, according to CDS 841503 $K_p$ 0.001% is applied [10] and implemented according to the methodology CSN EN 14387 [9]. The requirements of the standardized technical norms [5; 7; 8; 9] and the Czech defense standard [10] have been met in all tested filters.

3.2. Permeability of particular sizes of nanoparticles in measured range
The $K_p$ value has been measured and calculated in the whole range of our measurements for all tested filters.

3.2.1. Filter OF-90. Regarding the military filter, the highest permeability of the filter was measured for nanoparticle sizes from 100 to 200 nm, where the filter efficiency was 99.995%. The corresponding $K_p$ value of 0.005% in this range slightly exceeds the limit of 0.001% given by the standard [10]. This can be documented at the values shown in figure 4:

![Figure 4] Average permeability of particles in different sizes of particles – filter OF-90 (source:own)
3.2.2. Particle filters P3. For both particle filters, the highest permeability was also observed in the nanoparticle size range from 100 nm to 200 nm (see figure 5):

- the P3 filter had the lowest efficiency in this range at 99.995% (K_p 0.005%),
- the P3 filter with two threads had the lowest efficiency at 99.997% (K_p 0.003%).

![Figure 5](source:own)

Figure 5 Average permeability of particles in different sizes of particles – particle filters (source:own)

3.2.3. Filters MOF. The MOF-3 filter had the highest filter permeability for nanoparticles from 100 to 200 nm where the filter efficiency was 99.996% (K_p 0.004%). In contrast, the MOF-2, MOF-4 and MOF-5 filters had the highest throughput in nanoparticles ranging from 200 nm to 300 nm (see figure 6):

- the MOF-2 filter had the lowest efficiency in this range at 99.901% (K_p 0.030%),
- the MOF-4 filter had the lowest efficiency at 99.919% (K_p 0.081%, the value exceeds the limit given by technical norm [7]),
- the MOF-5 filter had the lowest efficiency at 99.930% (K_p 0.070%, this value exceeds the limit given by technical norm [7]).

![Figure 6](source:own)

Figure 6 Average permeability of particles in different sizes of particles – MOF filters (source:own)
3.2.4. **Filter FN a Health and safety filter.** Protective filters providing a high degree of penetration efficiency against nanoparticle permeability have been highly effective. Both of these filters had zero nanoparticle penetration and the capture efficiency was 100% in both cases.

4. **Conclusion**

In this research, the efficiency of the antiparticle filters introduced in the ACR and the protection of the population was carried out using ultra-fine aerosol of cupric oxide with a particle size in the range of 7.6 to 299.6 nm. The testing was carried out in the laboratories of the Institute of Analytical Chemistry of the Academy of Sciences of the Czech Republic. The test showed that although the experiment was carried out under modified conditions using an ultrafine cupric oxide aerosol, compared to the aerosol and the measuring range specified by standards [7; 10], the required maximum aerosol permeability coefficients for any of the tested filters were not exceeded. The recorded results indicate that the military filter and particle filters exhibited the highest aerosol permeability through the filters, especially in the nanoparticle size range between 100–200 nm, while the MOF protective filters had the highest permeability in the range of 200 to 300 nm. On the other hand, the FN filter and the Health and Safety filter, did not release CuONP particles at all and had 100% nanoparticle capture efficiency and were therefore the most effective. The results confirm that the worst efficiency of filtration is usually at the interface of applying different proportions of surface and depth filtration. The range of particle sizes that begin to be low for surface filtration and too high to be applied for the depth filtration mechanism is critical. The obtained results of the experiment indicate that the particles most subject to this effect are most often in the range of 100 to 200 nm.

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