ANALYSIS OF THE WAY TO INCREASE SAFETY IN TERMS OF POSSIBLE INHALATION OF NANO AND MICROPARTICLES DURING GUN SHOOTING

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Abstract

A firearm shot is a complicated physico-chemical process in where the by-product of the shot is a shot-fire product that contains both metallic and non-metallic micro and nanoparticles. The main aim of the experiment was to verify the efficiency of respirators against gunshot residues from pistol shooting on an indoor shooting range and testing the phytotoxicity of sediment particles taken from the shooting range floor. The experiments were focused on measuring their concentration of an observer (range 20-1000 nm) after gunshots residues (GSR) from pistol. The various types of respirators detected particles penetration. The efficiency was calculated from the measured values especially their FIT factor and S (%) - efficiency of protective equipment. The most efficient respirator was considered REFIL 651 (FIT factor = 93, S = 98.9. The samples from the shot fills were further tested on their phytotoxicity - a component of environmental toxicity. The test of phytotoxicity was conducted from specific places at a distance of 1 m and 3m from the boxes. The root growth inhibition *IC* (%) for 1 m was 65.84, for 2 m 75.08. The toxic effect of sediment particles might be considered high. The measurement proved the growth of nano- and microparticles by 3 digits in comparison to the standard in a normal atmosphere. The results should inspire the shooting range operators to extend the use of the personal protective equipment to respirators, along with hearing protectors and goggles and lastly to threat the deposit as a dangerous waste.

Keywords: Concentration of nanoparticles and micro particles, gunshot residue, respirators, FIT factor, phytotoxicity

1. INTRODUCTION

The paper follows up on the results of previous research measurements of aerosol micro- and nanoparticles of GSR when shooting at an indoor shooting range. This article enriches the tests of efficiency of respirators against the residues. The main aim of the experiment was to verify the efficiency of the five chosen respirators against GSR from pistol shooting on an indoor shooting range (FIT factor and S- efficiency of protective equipment) and also testing the phytotoxicity of sediment particles taken from the shooting range floor and lastly to recommend some safety measures for the operators. Detailed measurements during shooting with a pistol, submachine gun and a shotgun provided comprehensive data on the amount of nanoparticles, their weight and distribution [1,2]. The analysis of the samples established metallic particles including their distribution, always in relation to the type of firearm and ammunition [3]. The results showed the presence of nanoparticles of shot- fire products and therefore an increased risk (toxicity) for the shooters in areas with atmosphere polluted by GSR, either in gaseous or solid form. In order to prove the reduction of inhaled micro- and nanoparticles, an experiment was conducted, during which the observer were equipped with respirators and the concentration of nanoparticles was measured in front of and behind the respirator while shooting a pistol, which is the most frequently used firearm on the shooting range. At the same time samples of sediment particles were taken from the shooting range floor, to be tested for phytotoxicity - germination and root elongation test. The tests were conducted on seeds of white mustard (*Sinapis alba* L.).

2. EXPERIMENTAL PART

The "Patriot" indoor shooting range is located in Ostrava in a basement. The area available for shooting has internal dimensions of 33 x 4.5 m. The shooting post has dimensions of 25 x 4.4 m with 4 shooting boxes 1.1 m wide, see. Space for spectators (observers, instructors) is located behind the shooting zone, including a table, bench and cabinet. **The shooting** was conducted with a pistol: CZ 75 D Compact. **Ammunition**: 9 mm LUGER, SELLIER&BELLOT a.s. Lead bullet, nitrocellulose smokeless powder Vektan Ba-9 0.34 g. **Tested respirators:** Triosin T-500 (FFP -3), REFIL 641 (FFP-2), REFIL 651 (FFP-3), REFIL 731 (FFP-2), REFIL 711 (FFP-1). The marking in brackets specifies, as per EN 149, the penetration limit of the filter (Filtering Face Piece): FFP 3 (the lowest penetration), then FFP 2 followed by FFP 1 (the highest penetration). Measuring instruments: for measurement of carbon oxide concentration: GAS Detector MSA Orion Plus. For measurement and comparison of concentrations of nanoparticles in front of and behind a respirator PORTACOUNT Pro+ Fit Tester 8038 from TSI, measuring range 20-1000 nm. Protection factor, so-called FIT factor:

$$F = \frac{c_0}{c_1} \tag{1}$$

c_0 - concentration of pollutants outside the respirator, c_1 - concentration beneath the respirator, i.e. concentration entering the respiratory organ. FIT factor is a measure of efficiency of the protection of respiratory organs. The higher the *F* value, the safer the protective equipment for the user. Even though the *F* factor specifies how many times the particles concentration is reduced compared to the environment, sometimes it is more practical to use the expression "efficiency of protective equipment", *S* (%):

$$S = 100 - \frac{100}{F} \tag{2}$$

The tested person was an observer. He received the tested respirators, which were fitted with a hole for a sensor of particles concentration measurement. The shooter shot from the pistol at a target from the first box in intervals of app. 15 seconds. The observer stood behind the first box in the spectators' zone, app. 1.5 m from the shooting pistol. During a 7-minute cycle the observer performed, in one-minute intervals, 1. normal breathing, 2. deep breathing, 3. head from side to side, 4. head up and down, 5. speaking including grimaces, 6. bending at the waist, 7. normal breathing (exercises performed as per OSHA 29 CFR 1910.124, see **Figure 1**). The first measurement took place with the shooter with a unique respirator TRIOSIN T-500, but without exercises. The measurements for the REFIL 641 and 651 respirators were taken for the observer. For the duration of the experiment the shooter shot in regular intervals, one shot every 15 to 20 sec.

Figure 1 Course of exercises by the observer [L. Frishansova VUBP-Praha v.v.i.]

3. RESULTS AND DISCUSSION OF EFFICIENCY OF RESPIRATION

The results were processed in the table and graphics; the FIT factor and the efficiency of individual respirators was determined. The measured values of concentration of micro- and nanoparticles in the observers' area and behind the respirator tested by them are listed in **Table 1** together with the determined (calculated) FIT factors and the efficiency for the specific type of respirator. For clarity and quick orientation the number of particles in the observer's space is shown in graphics (**Figure 2**) for the individual type of experiment, and the FIT factor value as well (**Figure 3**).

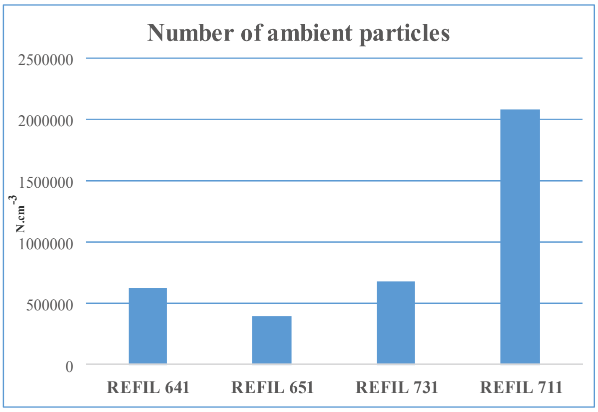

Figure 2 Graphical illustration of the number of particles in the area during individual tests in relation to the respirator type (observer)

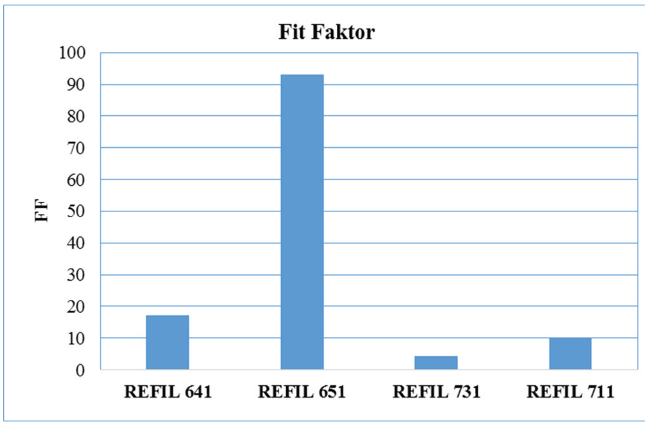

Figure 3 Graphical illustration of the F value in relation to the respirator type (observer)

The shooter was practically inhaling the particle values of the normal natural background. The *FIT* factor values are one of two measurements, without any exercises, so they do not comply with the OSHA 29 CFR 1910.134 standard in relation to the respirator quality (FFP value) and the *F* values, for the observer *F* is higher for the FFP1 respirator (REFIL 711) as compared to FFP2 (REFIL 731). The impact of different factors for the same types of respirators (**Table 1**) can be attributed to the effect of the respirator sealing [2] on the face of the observer and the shooter. We were interested in the effect of testing exercises on the *F* values and the respirator efficiency. The dependency of our experiments cannot be scientifically proved. The statistical reduction of the FIT factor and the efficiency is shown for exercise (bending at the waist).

Table 1 Overview of *FIT* factors and efficiency (*S*) of respirator in relation to the exercises

Test exercise**	**REFIL 641**		**REFIL 651**		**REFIL 731**		**REFIL 711**	
	F	**S (%)**	**F**	**S (%)**	**F**	**S (%)**	**F**	**S (%)**
1	28	96.4	261	99.6	7	85.7	8.3	87.9
2	49	97.9	183	99.4	2	50.0	9.7	89.7
3	20	95.0	109	99.1	5	80.0	12	91.6
4	20	95.0	117	99.1	6	83.3	12	91.6
5	19	94.7	67	98.5	4	75.0	7.6	86.8
6	7	85.7	51	98.0	3	66.6	13	92.3
7	15	93.3	77	98.7	3	66.6 or 60.6	11	90.9
Σ	17	94.1	93	98.9	4	75.0	10	90.0

4. RESULTS AND DISCUSSION ON TOXICITY IN THE ENVIRONMENT OF THE INDOOR SHOOTING RANGE DURING INTENSIVE SHOOTING

Along with an abnormal amount of micro and nanoparticles from the growth from 10^3 (background) to 10^6 during full shooting utilization of the shooting range we also measured the concentration of carbon oxide of app. 90 ppm, which is an allowable value for short-term intervention of professional firefighters. Along with carbon oxide, based on the study of the pyrolysis of nitrocellulose powder, other substances can be expected. In the quoted study [4] the mass spectrometer identified 26 pollutants: CO, NO, N_2O, CH_4, CO_2 and H_2O specified as primary, and acetylene, formaldehyde, acetonitrile, HCN, propene and ethylene oxide as secondary. These pollutants are not allied products for health. Establishing the composition and contents of metallic particles identified from volumes from atmospheres and identified by the EDAX system, including traction differentiation of particle sizes, were for shooting as follows Pb>Sb>Cu>Zn>Sn>Cd. Even though the weight of Pb particles in cm^3 was the greatest, particles with dimensions of 750-10000 nm prevailed. The weight of most nanoparticles up to 100nm was measured for Zn and Cu [3]. Lead poisoning has been known to mankind since antiquity; during the industrial revolution from the 18th century the situation deteriorated. Lead has no known biological function in organisms and when it enters the body it has a severe impact on health, which can be irreversible [5]:

- effect on nervous system, central as well as peripheral nervous system,
- impact on hemopoietin systems causes inhibition of vital enzymes (ALAD, ALA, enzyme catalyzing ferro chelatase - inserted Fe blocks the production of HEME (hemoglobin),
- nephrotoxicity - dysfunction of proximal porphyrin,
- cardiovascular effects,
- reproductive effects.

Lead is probably the most studied heavy metal. The primary location of lead deposits in the human body is the bones. The main mechanism of toxicity is the formation of ROS (formation of radicals •OH, •O2-, H_2O_2, H-O-O•). Depletion of reserves of antioxidants creates oxidative stress, which represents an imbalance between the production of free radicals and therefore the ability of biological systems to detoxify between products or to repair any damages. Free radicals will trigger a chain reaction, which leads to peroxidation of lipids, disturbance of cell oxidation of proteins and oxidation of nucleic acids (DNA, RNA) leading to cancer. Toxicity of so-called ion mechanism is caused by the lead's capacity to replace other ions $Cu^{2+,}$ $Mg^{2+,}$ Fe^{2+} and Na^+. This affects the basic biological processes in the body. The ion mechanism contributes to neurological deficit; after the calcium ion exchange the blood-brain barrier can be breached. Lead damages immature astroglial cells. The above-mentioned principle of ROS nanoparticles toxicity and oxidative stress applies also to so-called essential metals, which play an irreplaceable role in the bio organism. Zinc is necessary for the function of different mammal enzymes and it is present virtually in all plant and animal tissues [6]. The inhalation of vapors or fine dust of metallic Zinc and ZnO causes "brass founder's fever" (fever caused by metals and their oxides). It manifests itself as lethargy, headache, chest pain, irritating cough and it is accompanied by fever and temperatures up to 59 °C. The same applies to exposure to vapors of copper or its dust aerosols. Nano zinc and nano copper (and their oxides) are used for various industrial purposes (catalysts, polymer composites) and in healthcare. There are a number of research publications on the toxicity of metals and their oxides [7,8]. With results in vivo, as well as in vitro, including the test on human cells (liver, lung) and the phytotoxicity [9,10]. In essence, a certain level of genotoxicity based on ROS formation is always identified. Zinc oxide is in an ambivalent situation, because it has anti-bacterial properties and is applied as a composite of packaging of food [11] and its genotoxicity is used against carcinogenic cells [12,13]. The documented neuro-toxic effect of copper nanoparticles in the atmosphere can be viewed as an increased risk, by penetration through the skin and nose to soma sensory neurons in spinal ganglia [14].

4.1. Sediment toxicity on the indoor shooting range floor

The GSR are absorbed on different materials (clothing, skin, hair) and also sedimentation on surfaces within the shooting range. Phytotoxicity is an integral part of the environmental toxicity. Therefore the deposited particles were swept from the shooting range floor after a Czech Police shooting practice session and the surface particle collection and a germination and root growth test were conducted on *Sinapis alba* L. (white mustard) seeds according to relevant methodologies of determination of waste eco-toxicity. Introduced dust load into Petri dishes, pipetted 7mL of diluent, 20 seeds for germination stored in Petri dish with diluent at given temperature (20±2 °C), readout executed after 72 hours of germination out of reach of light. The ecotoxicity tests according to OECD Guidelines 208/1984, which is used as a standard test in Europe. Readout of keys according to relationship:

$$IC = \frac{(L_C - L_V)}{L_C} \cdot 100 \qquad (3)$$

IC is root growth inhibition (%), L_c arithmetic average of root length (mm), L_v arithmetic average of root length in tested media (mm).

The test of phytotoxicity was conducted from specific places with the area of an A4 paper sheet (210 x 297 mm), at a distance of 1 m and 3 m from the boxes. **Table 2** shows that the weight of the deposit of GSR grew on the shooting position with the distance from the shot. Also the toxic effect of sediment particles (see inhibition value) can be considered high.

Table 2 Weight gradient of the deposit in the shooting post and the box, including the specified inhibition of root growth

Distance from the deposit collection place (m)	Deposit collection point	Weight of deposit from area of A4 size (g)	Recalculation of deposit to m^2 (g)	Root growth inhibition IC (%)
1	Box 1	0.302	4.832	65.84
	Box 3	0.426	6.716	
3	Box 1	0.602	9.632	75.08
	Box 3	0.403	6.448	
0	Box 1	0.125	2.000	67.92
	Box 3	0.249	3.984	

5. CONCLUSION

The measurement showed the growth of nano- and microparticles by 3 digits in comparison to the standard in a normal atmosphere. This growth was caused by GSR particles, which, after partial chemical identification, can be included among toxic pollutants. The toxicity of the atmosphere on the shooting range is increased also by the high content of carbon monoxide. The results of our tests showed that the application of normal respirators substantially reduces the contents of inhaled particles. The measurement results should inspire the shooting range operators to extend the use of the personal protective equipment to respirators, along with hearing protectors and goggles. Especially for the instructors, who are exposed to shooting for extended periods. We can also conclude that the shooting results of our shooter were not affected by the use of the respirators. The shooter had no negative experience during shooting. The phytotoxicity showed the high toxicity of the deposit from GSR from the shooting range floor. The shooting range operators should remember this fact and treat the deposit as dangerous waste.

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