Experimental Survey Regarding the Dangerous Chemical Compounds from Military Polygons that Affect the Military Health and the Environment

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Activities specific to the military field, regarding the instruction process or the missions in the operating theatres, require military personnel to be exposed to a series of toxic chemical compounds, with effects ranging from short to long term. European legislation regarding environmental protection and employee health has become stricter and it directly influences the choice of materials that will be turned into ammunition. Most energetic materials from ammunition contain compounds whose synthesis and decomposition involves the release of high toxicity products into the environment. Shootings with classical weapons systems have an effect on the environment, in the shooting area and also in the place of impact with the objective, having both direct (the shock wave that results from the ammunition exploding, shrapnel, sound waves, high temperatures) and indirect (unexploded ammunition, contamination of the environment) effects. This paper presents the results of experimental research conducted in military shooting ranges during the testing of diverse smoke ammunition, in order to detect and identify the released chemical compounds, thus studying their impact on the fighters' health and security and evaluating the risks they pose on the environment.

Keywords: dangerous chemical compounds, smoke ammunition, toxicity, risk assessment

It has been recently ascertained an increase of the incidence of affections connected with professional exposure to: industrial toxic substance, fuels, combustion products resulted from explosions, ammunition usage, pyrotechnical substances, fuel burning or fires, decontamination products, pollutants, particles from atmosphere or waste from all categories.

These activities produce, besides the effects upon the soldiers2 health, some effects upon the environment, effects that have to be assessed because they affect the population2 s health in the area as well. The working conditions for these substances should be studied carefully so that accidents could be avoided and operations must be carried out on optimum security level.

Most NATO and EU state members have become aware of the necessity of implementing the measures which have to provide the lowest impact upon the environment during military activities of training and defense.

A complex environment legislation with regard to fabrication and usage of chemical substances as well as the storage of chemical substance wastes is rapidly expanding all over the world. REACH Directions (Directions regarding recording, assessment, authorization and restriction of chemical substances), RoHS Directive (Restriction of Hazardous Substances Directive 2002/95/EC) and other directives impose more and more restrictions and regulations in this field [1].

Nations and implicitly their armies are more and more concerned about aspects related to environment, work security and health in armament production, usage and disposal, being ready to assume high costs in producing environmentally friendly ammunition, waste disposing, decontamination and recondition of the fire range locations. The concerns regarding work security and health are fundamental in activities carried out in the military testing and training fields, requiring profound knowledge of the products used, procedures and equipment; nobody can work safely unless physical and chemical properties of the substances used are known as well as their behavior, the conditions in which they can decompose, the decomposition way, the effects of explosion, means of protection and intervention and first-aid measures [2].

As we cannot speak about absolute security, taking care of the human factor in all the sectors of production activity has to be preponderant. It is necessary to continuously increase the security level in terms of people and their activity while at the same time respecting the technical, managerial, economic, and research requirements to ensure the best possible level of the entire production process [3-16]. For this reason it is necessary to establish and apply some adequate measures to control the risks that occur in such situations, to limit their effects and apply specific medical countermeasures in order to prevent and treat the affections with invalidating potential that can also have long-term impact upon military life quality as well as upon the environment.

Regarding the categories of substances found in the military fields, in the firing ranges are carried out different types of trainings and testing activities with armament and ammunition from endowment or being in different stages of development.

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Presence of energetic materials and metals in ammunition cannot be avoided and this represents a permanent risk of air, soil and water pollution. Energetic materials represent a special risk for the environment due to their dangerous toxicological, physical and chemical properties.

During operation or demilitarization of a pyrotechnic system, a combustion reaction occurs and afterwards the reactants (fuel, oxidizer, binder, and additive) change into reaction products (gaseous or solid) which can present risks of toxicity.

Gaseous products at high pressures and temperatures results from powder burning and in some cases a reduced quantity of solid products could be also formed. Composition of the burning products depends on the nature of the powders and their burning conditions as well [1]:

-when burning some powders based on nitrocellulose the main gaseous products are: carbon dioxide and monoxide, nitrogen and water. In certain situations the gaseous products can contain methane, hydrocyanic acid and nitrogen oxides (under normal burning conditions they can form in small quantities);

-when burning some powders based on mixtures of compounds, the resulting products are: carbon dioxide and monoxide, nitrogen oxides, water as well as a series of other compounds, depending on the nature of mixtures;

-when burning black powders made from nitrates (sodium or sometimes potassium nitrates), sulfur and coal, the main gaseous formed products are carbon dioxide and monoxide, nitrogen.

The burning products of fuels and oxidizers contain different quantities of metallic oxides (magnesium, aluminum, potassium, beryllium, zirconium, iron, etc.), nitrogen oxides, ammonia, halogens (fluorine, chlorine), carbon dioxide and monoxide, etc., as well as a series of solid particles having different sizes which can be inhaled by the staff working with the armament system or can contaminate the soil and surface water.

During operation, the explosive compounds get into the environment and can contaminate the soil, the surface water and underground water. In time, these substances are transformed by processes such as photolysis, hydrolysis, reduction, biodegradation into compounds like: aromatic nitro-compounds, nitrates esters, nitramines [17,18], oxidizing substances such as nitrates, chlorates, perchlorates, bromates, etc.

Statistics show that about 5% of the fired ammunition during training firings remains unexploded. The main problem is represented by the fact that toxic substances get on the soil [19-38], both directly and indirectly (through water and air). If these pollutants are soluble, they are transported by water through the soil and they can get into the groundwater, affecting the living organisms: plants, animals, and humans, first of all by modifying their natural characteristics, especially their content in active principles [37-45]. Figure 1 presents a model of the pollutants linkage [40].

Assessment of ammunition impact upon the environment is difficult regarding the measurement of the burning products and released waste. Usually gaseous products and solid wastes are determined, the monitored toxic products being: CO, CO_2, NO_x, HCN, NH_3, PAH, dioxines, metals, $PM_{2,5}$, PM_{10} and unburned energetic materials.

Experimental part

Determining the toxicity of the gaseous reaction products resulting from the use or destruction of an explosive material /ammunition may be achieved by identifying the components and determining their concentration. Experimental determinations were carried out when operating several types of CBRN ammunitions, from smoke ammunition: smoke candle LF-2 and LF-12 and smoke grenade with white smoke (white GF).

Samples were taken and the following types of determinations were performed:

-*on site* determination of the reaction products, nature and concentration, generated during CBRN ammunition operation;

-*on site* determination of the particle concentration in the air during CBRN ammunition operation;

-elemental chemical mapping, dimensional analysis of aerosol particles, identification of compounds from solid waste/aerosols.

Results and discussions

Determination of the reaction products, nature and concentration, generated during CBRN ammunition operation

The different types of gases were determined by direct measurements, on the spot, using two MiniWarn gas analyzers equipped with electrochemical sensors. The determinations aimed to identify the maximum concentration of substances by placing the analyzers in the area where the smoke density was at the maximum level. When performing the determinations, the cumulative effect was also monitored by the operation of several ammunitions at the same time (fig. 2).

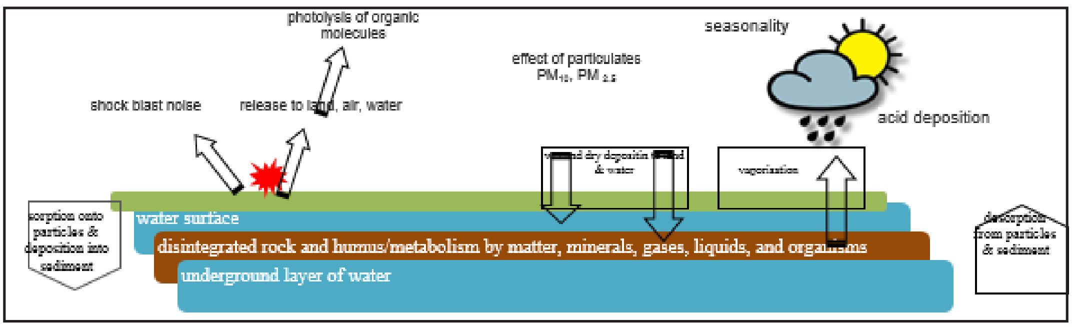

Fig. 1. Pollutants linkage model

a) LF-12 b) LF-2 c) White GF

Fig. 2.Image during the operation of smoke ammunition

Tested ammunition	Atmospheric conditions			Maximum concentration (ppm)					
	Wind speed (m/s)	Temp. (^{0}C)	Humidity (%)	HCN	NO	NO_2	CO	CO_2	Cl_2
1 pc. LF-12	1÷2	31.5	49	1.4	-	-	27	-	-
2 pcs. LF-12	2÷5	32.1	59	2.3	-	-	21	-	-
5 pcs. LF-12	2÷4	28.5	61	5.4	3	-	72	-	-
1 pc. LF-2	2÷4	28.5	61	-	0.4	0.1	6	-	0.1
5 pcs. LF-2	2÷3	31.8	51	-	2.2	0.6	26	-	0.5
1 pc. white GF	2÷5	20.8	71	-	0.1	0.2	10	-	0.3
5 pcs. white GF	2÷4	32.9	51	-	0.5	0.5	4	-	0.9

Table 1
MAXIMUM CONCENTRATION OF SUBSTANCES, DETERMINED DURING TESTED AMMUNITION OPERATION

Table 1 shows the results of the measurements and atmospheric conditions recorded at that time. The masking effect is closely related to the amount of solid products generated per unit time when using the pyrotechnic system.

Determination of particles concentration in air, identification of compounds from solid waste/aerosols and their dimensional distribution analysis

Determinations were carried out for particle concentration in the air using the Tecora's ECHO PM sampling system, with sampling head for total suspended particles (TSP) and glass fiber filters.

The solid residues resulted from ammunition have been collected on adhesive carbon disks, specially used in electronic microscopy. Toxicity level of the solid particles for the human body was determined both by the chemical nature and by the dimensional characteristics (particle diameter) and their rate of deposition on the human respiratory system. The samples taken were investigated by scanning electron microscopy (SEM) by surface chemical mapping, using a VEGA II LMU TESCAN microscope coupled with Bruker QUANTAX 2000 EDX detector, with the following parameters: accelerating voltage -30 kV; working time: 1200 s; scanning speed: 0.4 kcps.

LF-12 testing

Determinations were performed for two smoke candles weighting approx. 12.5 kg. Particle sampling was performed at a height of 1 m and 30 m epicenter distance, for 10 min. Table 2 shows the relative concentration of chemical elements, normalized to unity for the investigated area. Figures 3 and 4 show the elemental chemical mapping and the spectra of chemical elements identified from LF-12 smoke candle samples.

Table 2
CONCENTRATIONS OF ELEMENTS IDENTIFIED WITH SEM-EDX IN CASE OF LF-12-TESTING

K	Al	Zn	Ba	Pb	Cl
1.50	1.49	12.11	2.86	1.12	10.64

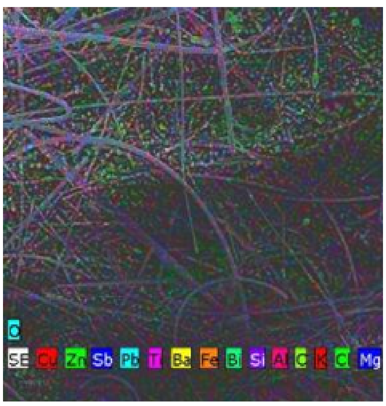

Fig. 3. Elemental chemical mapping in the case of LF-12 testing

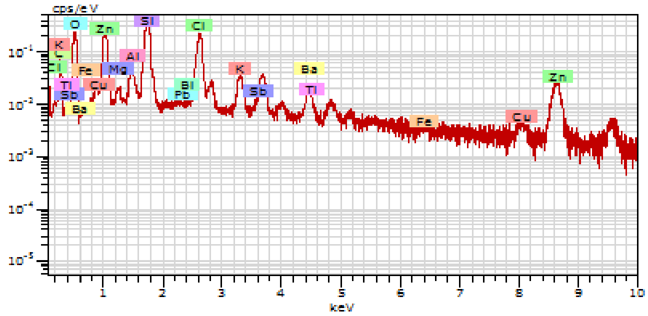

Fig. 4.Spectra of chemical elements identified

LF-2 testing

LF-2 shows the same pyrotechnic chemical composition, but gauge size smaller than LF-12, weighting approx.2 kg, which means the proportional reduction of the smoke screen dimensions. During testing, samples were collected at a height of 1 m and 7 m epicenter distance, for 10 min. Table 3 shows the relative concentration of chemical elements, normalized to unity for the investigated area, and table 5 shows the particle concentration in the air. Figures 5-6 show the elemental chemical mapping and the spectra of chemical elements identified from LF-2 smoke candle samples.

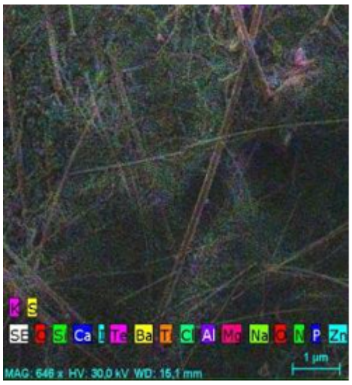

Fig. 5. Elemental chemical mapping in the case of LF-2 testing

Table 3
CONCENTRATION OF ELEMENTS IDENTIFIED WITH SEM-EDX IN THE CASE OF LF-2 TESTING

K	Al	Zn	Ba	Pb	Ca	Cl
1.26	1.19	2.31	2.19	1.92	1.02	12.82

White GF testing

White smoke candle is part of the masking effect ammunitions, weighting approx. 0.8 kg pyrotechnic charge. During testing, samples were collected at a height of 1 m and 7 m epicenter distance for 15 min. Table 4 shows the relative concentration of chemical elements, normalized to unity for the investigated area, and table 5 shows the particle concentration in the air.

Analysing the results of these measurements (table 1-5), some important points have to be observed:

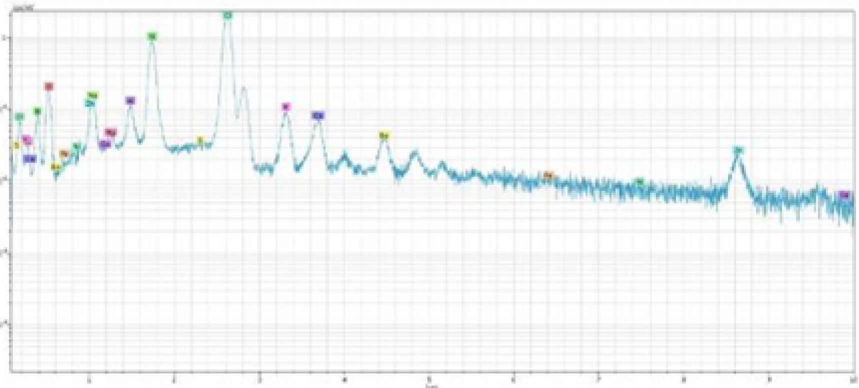

Fig. 6.Spectra of chemical elements identified

Table 4
CONCENTRATION (%) OF ELEMENTS IDENTIFIED WITH SEM-EDX IN THE CASE OF WHITE GF TESTING

K	Zn	Ba	Ca	Mg	Cl
1.72	1.62	1.12	0.18	0.10	5.82

Table 5
CONCENTRATION OF PARTICLE IN THE AIR

Tested ammunition	Atmospheric conditions			Determined concentration
	Wind speed (m/s)	Temperature (^{0}C)	Humidity %	(mg / m^3)
2 pcs. LF-12	2÷4	32.1	59	69.24
2 pcs. LF-2	2÷5	20.8	71	24.21
White GF	2÷4	26	69	16.10

-The selectivity and the accuracy of the *on site* measurements support the idea of using electrochemical sensors for the qualitative and quantitative identification of gas products created during the pyrotechnic combustion of the components.

-The air pollutants resulted from the use of the tested ammunitions have concentrations close to the limits prescribed by current laws, however, they do not exceed these limits in the given time interval.

-We note that the cumulative effect obtained through the use of several smoke ammunitions simultaneously leads to dangerous concentrations, if the personnel are exposed to them without protection equipment, for a longer period of time.

-The legal concentration limit for ZnO based smoke is 10 mg/m^3 for a 15 min interval, which means that the concentrations derived from the use of smoke ammunitions become dangerous, either by extended exposure or by using more of them at the same time.

-In the case of LF-12, the concentration of the particles in the air reached a very high value (69.24 mg/m^3) and the dimensional distribution of the particle inside the 0.1 μm interval was at 2%, value representing the percentage of particles that will be absorbed by the lungs.

Conclusions

Reducing the impact that shooting activities and military instructions/trainings have on the environment can be achieved through: using more ecological materials, replacing the chemical compounds in classical ammunition with lower toxicity compounds, smart handling of the products created by these activities in order to control the contamination and facilitate the soil recovery, detecting and eliminating unexploded ammunition etc.

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