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FIREFIGHTERS' PROTECTIVE CLOTHING – WATER CLEANING METHOD VS LIQUID CO_2 METHOD IN ASPECT OF EFFICIENCY

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Abstract
Multilayer material of firefighters' Personal Protective Equipment (PPE) creates obstacles in toxins disposal while washing. This leads to long-term exposure and health risks to firefighters. The University of Leuven conducted experiments that showed the highest concentrations of toxins in the bodies of firefighters who wore the most contaminated clothes. In contrast a non considerable increase of toxins was observed in the group using LCO_2 decontaminated clothes. Another study run in Finland in 2018 analyzed water cleaning of PPE and concluded that it was not efficient in providing safe and clean firefighters' clothing. To check the efficiency of LCO_2 cleaning, a set of laboratory tests on worn-out Polish fire gear was undertaken. The results presented in this paper confirmed that the clothes were clean enough to consider them safe for use.

Keywords: **Firefighters' clothing cleaning; Firefighters' clothing decontamination; Firefighters' PPE, Firefighters' protective clothing; Liquid CO_2 firefighters' clothing decontamination.**

1. INTRODUCTION

Although, firefighters would appear to be well-equipped when it comes to self-protection, the matter of cleaning their Personal Protection Equipment (PPE) is a subject that needs further research. In the event of fire, many toxic substances are created, including polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and other substances that accumulate in the body [8, 13, 1, 12].

It has been proven that the multilayer structure of the protective clothing of firefighters creates obstacles for effective disposal of toxic substances that contaminate this clothing [9, 6]. This may result in a great risk of developing different illnesses among firefighters due to cyclical exposure to these substances [15, 11, 3]. For this reason, it is found highly important to clean firefighters protective clothing properly [1, 7].

In firefighting terminology, cleaning and decontamination are often used as synonyms. However, it should be noted that there is a significant difference between cleaning, which is more general, and decontamination, which is a more specific concept [16]. In the case of decontamination of firefighter clothing, it must be ensured that the undesirable substances are below the limit set by the relevant guidelines and standards. This helps ensure that the clothing is considered safe for health and proper use [4, 18, 19]. Currently, firefighters clothing is not covered by decontamination standards, and the level of impurities contained are not measured. The clothes are only assessed visually.

In Poland, as with other countries, firefighters' protective clothing is washed in water with detergents. For this purpose, washing machines are provided in fire brigade stations [1]. These are often standard washing machines – although increasing use of more sophisticated machines, consisting of water washing machines and specialized dryers, can be found. Some headquarters use industrial laundry services. Very rarely, but unfortunately there are cases when firefighters' protective clothing is washed in private homes. It should be acknowledged that the environment in which contaminated firefighters' protective clothes are unpacked and transferred to washing machines, will become contaminated. Harmful substances that settle on the various surfaces in the laundry rooms and inside the washing machines can spread to the clothes of others [10].

A Report from a study run by the Finnish Institute of Occupational Health, the National Institute of Health and Welfare of Finland, and the Dutch Institute for Occupational Safety (IFV) showed the low effectiveness of most widely used cleaning method of firefighters clothing using water cleaning [14]. This study shows that, despite the use of intensive water washing in specialist appliances, the washing efficiency of more than 40 per cent is not achieved. It should be noted that the washing temperature used for the study was 60°C, which is above the recommendations. However, this method of cleaning is widely considered sufficient. The study showed that the levels of PAHs and other harmful substances in the materials of firefighters' multi-layer clothing after water cleaning are exceeded. The average concentration of total PAHs in different samples of the multilayer material, in one of the tested jackets after water cleaning, was up to 550 ng/cm^2. Furthermore, the average concentrations and standard deviations of a total of 18 PAH in contaminated firefighters' jackets after water cleaning exceeded the limit value of 250 ng/cm^2 established in the GS Mark procedure. The GS Mark is a seal of approval for "Geprüfte Sicherheit". The Mark demonstrates that the product was tested for safety of use conducted by an officially recognized testing centre. It is regulated by German law (German Product Safety Act).

The authors of the study also stated that due to the fact that measurement results of harmful substances in the samples of the material tested after washing exceeded the permissible limits, other methods of removing contaminants from firefighter clothing should also be considered, such as ozonation, treatment with liquid carbon dioxide or a combination of both of these methods [14].

The University of Leuven carried out an experiment on three groups of firefighters: one group wore contaminated protective clothing without washing, one wore contaminated protective clothing cleaned by industrial laundry (ISO 15797-2), and the last group wore contaminated protective clothing cleaned with liquid CO_2 method. During the study, and blood tests were performed to detect the presence of toxic substances in the firefighters' bodies. Firefighters who wore the most contaminated clothes had the highest concentrations of harmful substances per mole of creatinine in their and blood. The second highest results were obtained in the group whose clothes were washed in an industrial laundry. In the group whose clothes were decontaminated using the liquid CO_2 method, there was no significant increase in toxic substances in urine and blood during the entire study period [20].

To prove the efficiency of the liquid CO_2 cleaning method, a test has been carried out on worn-out firefighter protective clothing. The samples were taken for testing from the clothing before and after decontamination with the LCO_2 method.

2. MATERIALS AND METHODS

The firefighters' protective clothing handed over for testing was produced by LION LHD Group Deutschland GMBH from Köln. It was produced in November 2013, model VVKB164404, size M/S. Multilayer clothing consisted of: the outer layer (woven fabric – 59 per cent paraaramid, 39 per cent PBI, 2 per cent antistatic), moisture barrier (bicomponent membrane based on PTFE) laminated to thermal insulation layer (nonwoven fabric – 100 per cent aramid) and the lining (woven fabric – 50 per cent aramid, 50 per cent Viscose FR). Photos of the tested firefighters' protective clothing is presented in Fig. 1a and 1b.

The tested clothing was used regularly for different kinds of fires and hazards for several years by a Polish firefighter and fire instructor. This garment was washed regularly using a water cleaning industrial unit and a drying machine at the local fire station. When it was handed over to the CENTEXBEL laboratory in Belgium, the clothing was considered basically worn out. The clothing was not washed before sending it to the laboratory for testing.

At first, the representative samples of the external layer, membrane and lining, were subjected to ultrasonic extraction in toluene and then analyzed for

Figure 1a.
The tested firefighters' protective clothing (Analysis Report 21.00160.01)

Figure 1b.
The tested firefighters' protective clothing (Analysis Report 21.00160.01)

Figure 1c.
The tested firefighters' protective clothing (Analysis Report 21.00160.01)

polycyclic aromatic hydrocarbons (PAHs) content. This made use of gas chromatography techniques with a mass-selective detector (GC-MSD). The research was carried out in accordance with the procedure AFPS GS 2014 (AfPS GS 2019:01 PAK, 2020).

Subsequently, the tested firefighters' clothing was sent to DECONTEX Benelux in Tielt for industrial cleaning according to the DECONTEX TECHNOLOGY® and sent back to CENTEXBEL laboratory for further testing of materials for toxic substances.

The cleaning process carried out at DECONTEX was conducted with liquid CO_2 under a pressure of 53 bar. Under such high pressure, the liquid CO_2 penetrated the fibres of the multi-layer structure at a temperature of 22°C, loosening all the substances trapped in the materials of the multilayer clothing. In this way, the harmful substances particles contained in the contaminated clothing were removed with compressed CO_2. After this phase, samples of materials were taken from the LCO_2 cleaned protective clothing. These samples were tested using ultrasonic extraction with toluene and GCMS-MS as the analytical method used for the first testing. The samples were rechecked for polycyclic aromatic hydrocarbons (PAHs) content in the outer layer, membrane, and lining. The lower limit of all the contaminants detection was 0.200 mg/kg except for benzofluoranthenes with the limit of 0.600 mg/kg.

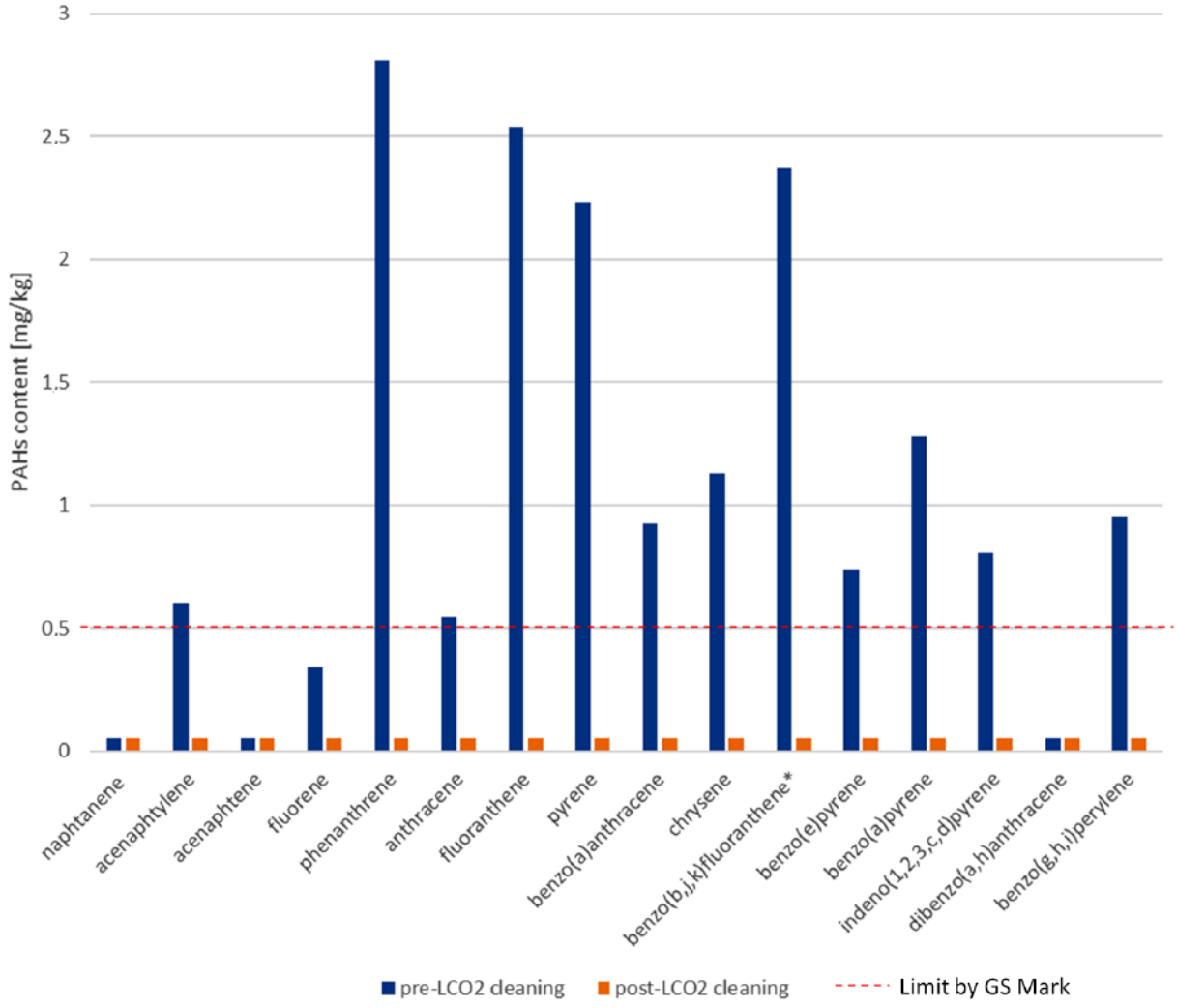

Figure 2.
PAH content in the outer layer of the protective clothing before and after using liquid CO_2 cleaning technology (Analysis Report 21.00160.01)

3. RESULTS

In Figure 2, the content of the PAHs in the external layer of the protective clothing before cleaning is shown in blue. The orange bars show the results obtained for samples of the outer clothing layer after cleaning in liquid CO_2. The dashed line shows the reference limit in GS Mark.

The total level of PAHs in the external layer before cleaning was 17.3 mg/kg on average. After cleaning in LCO_2, the total PAH result became below the lower limit of detection (<0.200 mg/kg). As shown in Fig. 2, the reference limit of the GS Mark was exceeded in most of the PAHs tested before cleaning the clothing. However, after liquid CO_2 cleaning, the result in the outer layer was below the reporting limit of the device used in the laboratory (<0.200 mg/kg).

As shown in Fig. 3, the highest results of PAHs content in protective clothing were observed in the membrane layer. Before cleaning, some PAH levels were up to 9 mg/kg, when the reference limit by the GS Mark is 0.5 mg/kg. Eight out of 16 PAHs tested in membrane samples before LCO_2 cleaning show values above the reference limit by the GS Mark. Again, after liquid CO_2 cleaning, all PAHs tested in membrane samples were below the reporting limits (<0.200mg/kg).

The sum of PAHs in the membrane before cleaning the gear in LCO_2 was 29.5 mg/kg. After cleaning, the total PAH result in the membrane was below the

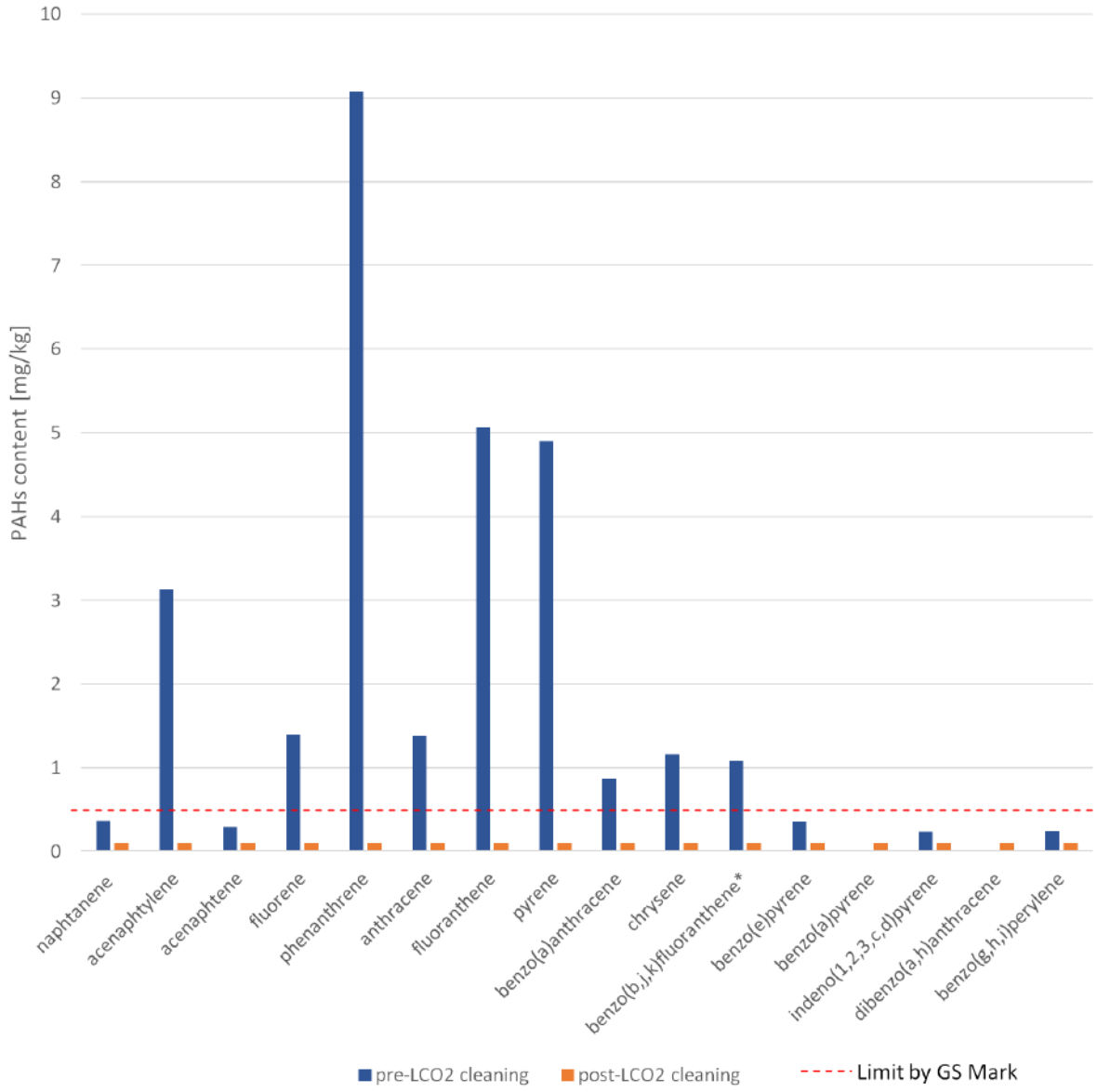

Figure 3.
PAHs content in the membrane of the protective clothing before and after using liquid CO_2 cleaning technology (Analysis Report 21.00160.01)

reporting limit of the device used in the laboratory (<0.200 mg/kg).

Fig. 4 shows the PAH content in the lining before and after liquid CO_2 cleaning the gear. The sum of PAHs before cleaning was 1.76 mg/kg. After cleaning, the sum of PAHs in the lining was below the reporting limit of the device used in the laboratory (<0.200 mg/kg).

As shown in Fig. 4, the reference limit of GS Mark was exceeded once in the PAHs tested before cleaning the protective clothing – for phenanthrene. Whereas, after liquid CO_2 cleaning, the results for the lining were below the reporting limit of the device used in the laboratory (<0.200 mg/kg).

As this testing shows, liquid CO_2 technology used for cleaning the contaminated firefighters' gear is very effective. The values obtained from the tests after this procedure show that all tested layers of protective clothing are clean enough to consider it safe for use as it comes to PAHs content. The reference limits were not exceeded in any of the tests after LCO_2 cleaning. Moreover, none of the PAHs tested in the samples in any of the layers exceeded the reporting limit of the device used in the laboratory.

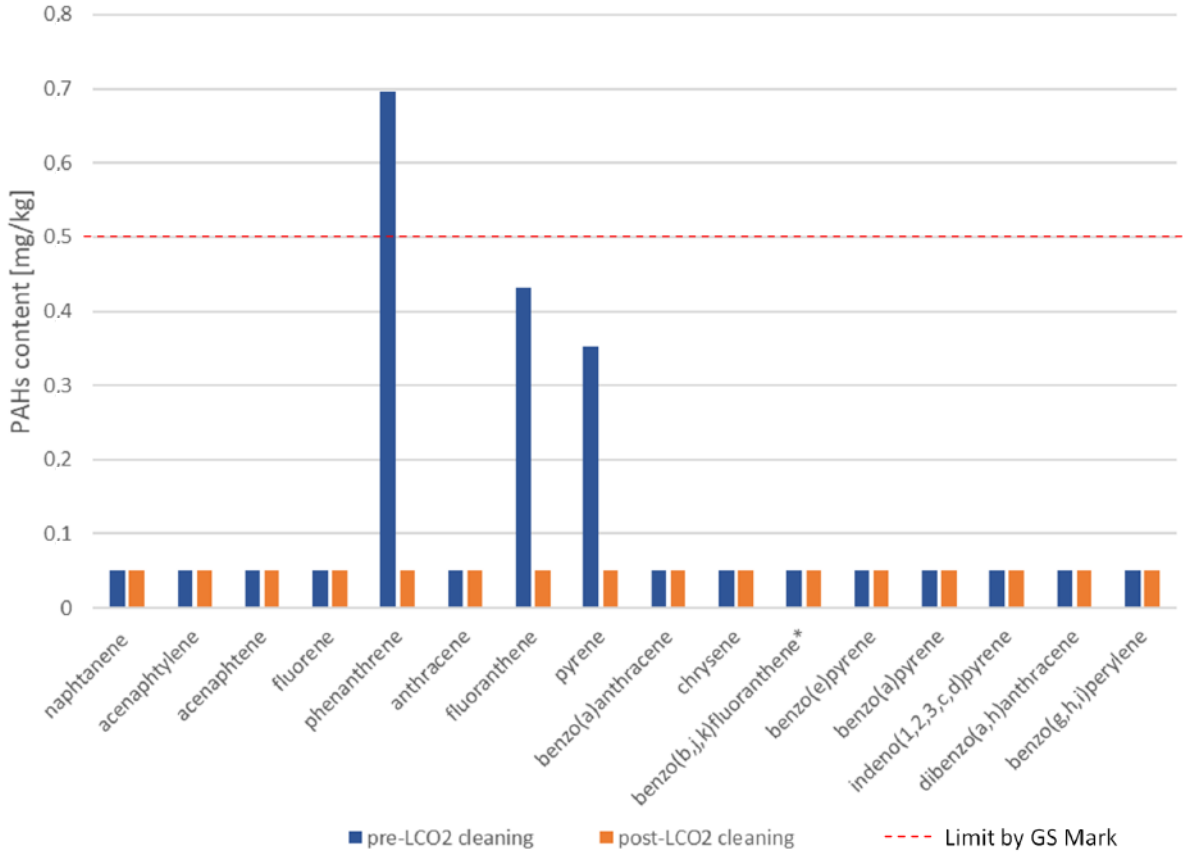

Figure 4.
PAHs content in lining of the protective clothing before and after using liquid CO_2 cleaning technology (Analysis Report 21.00160.01)

4. DISCUSSION AND CONCLUSIONS

The paper presents differences between cleaning and decontamination effectiveness of the protective clothing of firefighters. The term "cleaning" refers to the removal of contaminants that are visible to the naked eye. The term "decontamination" covers the effective removal from protective clothing of substances harmful to the user, which are not visible to the naked eye. Decontamination is a much narrower concept that requires compliance with a number of requirements.

Studies carried out in Finland [14] showed that, despite intensive washing of firefighters clothing in specialist appliances, using the water cleaning method, washing efficiency of more than 40 per cent is not achieved. Although the process of washing firefighters' protective clothing was carried out in accordance with detergent and washing machines producers' guidelines, a significant amount of toxic substances were detected in the layers of this clothing after washing.

Contact with fire residues in the contaminated clothing leads to the deposition of harmful substances in the firefighters' body through long and repeated exposure through the skin and breath, especially in the case of polycyclic aromatic hydrocarbons [5]. Therefore, exposure to harmful substances should be avoided.

Until there are effective and widely available decontamination technologies in place, other guidelines should be followed that can help reduce exposure to harmful substances. Protective clothing should be taken off during breaks to avoid unnecessary exposure to fire residues emitted from contaminated clothing. It is highly recommended that liquid CO_2 cleaning should be taken into consideration to decontaminate the clothing at least twice a year due to the planned check-up of the PPE. This will reduce the exposure of the firefighter to harmful toxins in the clothing. It is also highly advisable to use LCO_2 technology after incidents where contamination is likely. As shown above, cleaning PPE in liquid CO_2 enables the removal of the PAH contained in the structure of

the materials to a level that is not reported by the laboratory devices.

The methods currently used for firefighters' PPE cleaning show low effectiveness, whereas some other novel technologies can prove to be effective. However, their wider implementation would require considerable costs. Future research should be directed towards gaining more expertise in the field to develop the best recommendations for washing PPE, considering both the effectiveness of cleaning and the economic considerations.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interest.

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