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POLYCYCLIC AROMATIC HYDROCARBONS IN FIREFIGHTERS: ATTITUDES, DEPOSITION AND DECONTAMINATION OF PROXIMITY FIREFIGHTING PROTECTIVE CLOTHING

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Polycyclic Aromatic Hydrocarbons in firefighters: attitudes, deposition and decontamination of proximity firefighting protective clothing

Thesis submitted in fulfillment of the requirements for the degree of Ph.D. in Chemistry in the postgraduate program in chemistry.

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Hidrocarbonetos Policíclicos Aromáticos em Bombeiros: Atitudes, Deposição e Descontaminação de Roupa de Aproximação para Combate a Incêndio

Tese apresentada em cumprimento dos requisitos para o grau de Doutor em Química no Programa de Pós-graduação em Química.

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I dedicate this work to the love of my life,
my grandfather, Antônio José Marcelino.

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LIST OF ABBREVIATIONS

9MA - 9-methylanthracene
ANOVA - Analysis of Variance
AOPs - Advanced Oxidative Processes
ASTM - American Society for Testing and Materials
ATSDR - Agency for Toxic Substances and Disease Registry
ATR/FTIR - Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance
BEPH - bis(2-ethylhexylphthalate
BLK - Blank, without the light irradiation
BTEX - Benzene, Toluene, Ethylbenzene and Xylene
CBMDF - Corpo de Bombeiros Militares do Distrito Federal (Federal District Military Fire Department)
CBMPE - Corpo de Bombeiros Militares de Pernambuco (Pernambuco Military Fire Department)
CETOP - Centro de Treinamento Operacional do Corpo de Bombeiros Militar do Distrito Federal (Operational Training Center of the Military Fire Department of the Federal District)
CONAMA - Conselho Nacional do Meio Ambiente
Decon - Decontamination
FF - Firefighter
FTIR - Fourier Transform Infrared Spectroscopy
GC - Gas Chromatography
GC/MS - Gas Chromatograph coupled with a Mass Spectrometer
H-NMR - Nuclear Magnetic Resonance Spectroscopy
HPLC - High-Performance Liquid Chromatography
IARC - International Agency for Research on Cancer
ISO - International Organization for Standardization
LOD - Limit of Detection
LOQ - Limit of Quantification
MRLs - Minimal Risk Levels
MS - Mass Spectrometry
NFPA - National Fire Protection Association
PAHs - Polycyclic Aromatic Hydrocarbons
PCBs - Polychlorinated Biphenyls
PCDDs - Polychlorinated Dibenzodioxins
PCDFs - Polychlorinated Dibenzofurans
PFPC - Proximity Firefighting Protective Clothing
$PM_{2.5}$ - Particles smaller than 2.5 micrometers

POPs - Persistent Prganic Pollutants

PPE - Personal Protective Equipment

Proximity Firefighting Protective Clothing

PYR - Pyrene

SCBA - Self-Contained Breathing Apparatus

SEM/EDS - Scanning Electron Microscopy with Energy Dispersive X-Ray Spectrometry

SS - Standard Solution

SVOCs - Semi-volatile Organic Compounds

TMS - Tetramethylsilane

ULP - UV Lamp Photolysis

USA - United States of America

USEPA - the United States Environmental Protection Agency

UV/VIS - Ultraviolet–visible spectroscopy

VOCs - volatile organic compounds

VVOCs - Very Volatile Organic Compounds

WHO - World Health Organization

WLP - White Lamp Photolysis

ABSTRACT

The presence of polycyclic aromatic hydrocarbons (PAHs) in firefighters' personal protective equipment is a concern. PAHs are compounds that have two or more condensed aromatic rings and are considered carcinogenic, mutagenic, and teratogenic. Several studies have shown that occupational exposure of these professionals to toxic compounds increases the risk of developing cancer, and other diseases. Some habits, such as adequate storage, washing method and washing frequency, can reduce this risk. With that in mind, we developed a form to assess attitudes and working practices of firefighters from *Distrito Federal* and *Pernambuco* related to the presence of these pollutants in personal protective equipment. The results show good awareness level from firefighters related to health attitudes, but, on the other hand, it was evidenced the lack of structure inside fire departments, making more difficult to adopt good habits that could reduce the exposure to carcinogenic compounds.

Besides that, we also evaluated the presence of PAHs deposited in firefighters' personal protective equipment during training exercise. Samples were collected after a firefighting training exercise and analysis were done with gas chromatography coupled to mass spectrometry. A set of 16 PAH were searched and 8 were found in samples that were collected in several point in firefighters´ protective equipment. The highest concentration and variety of pollutants was found at an instructor, very probably due to the higher exposure frequency compared to those firefighters who carry out one-off combats.

Finally, we have evaluated some methods to decontaminating firefighters' fire-fighting suits. Photolysis with an ultraviolet and white lamp were evaluated, as well as the addition of an oxidizing agent (H_2O_2) to oxidize two probe PAHs. Regarding the fibers, damage was verified by scanning electron microscopy, optical microscopy and attenuated total reflection Fourier transform infrared spectroscopy. In addition, a tear resistance test (ASTM D2261) was performed on the outer layer fabric of the jacket. Best result was achieved using white lamp photolysis (WLP), when it was possible to remove more than 83% of the pyrene and 9-methylanthracene previously deposited. The WLP was compared with the most used techniques (washing in a washing machine and brushing with soap and water) and showed better results. With this, it was possible to develop a simple and inexpensive method of decontamination based on photolysis, which is effective in the degradation of PAHs, in addition to maintaining the integrity of Kevlar® and Nomex® fibers.

Keywords: Polycyclic aromatic hydrocarbons, advanced oxidative processes, photolysis, fire residues, and firefighting clothing.

RESUMO

A presença de hidrocarbonetos policíclicos aromáticos (HPA) nos equipamentos de proteção individual dos bombeiros é preocupante. HPAs são compostos que possuem dois ou mais anéis aromáticos condensados e são considerados cancerígenos, mutagênicos e teratogênicos. Diversos estudos têm demonstrado que a exposição ocupacional desses profissionais a compostos tóxicos aumenta o risco de desenvolver câncer e outras doenças. Alguns hábitos, como armazenamento adequado, método de lavagem e frequência de lavagem, podem reduzir esse risco. Pensando nisso, desenvolvemos um formulário para avaliar atitudes e práticas de trabalho dos bombeiros do Distrito Federal e de Pernambuco em relação à presença desses poluentes em equipamentos de proteção individual. Os resultados mostram um bom nível de conscientização dos bombeiros em relação às atitudes de saúde, mas, por outro lado, foi evidenciada a falta de estrutura dentro dos corpos de bombeiros, dificultando a adoção de bons hábitos que pudessem reduzir a exposição a compostos cancerígenos.

Além disso, também avaliamos a presença de HPAs depositados nos equipamentos de proteção individual dos bombeiros durante o exercício de treinamento. As amostras foram coletadas após exercício de treinamento de combate a incêndio e as análises foram feitas por cromatografia gasosa acoplada à espectrometria de massas. Foram pesquisados um conjunto de 16 HPAs e encontrados 8 em amostras coletadas em diversos pontos dos equipamentos de proteção dos bombeiros. A maior concentração e variedade de poluentes foi encontrada em um instrutor, muito provavelmente pela maior frequência de exposição em relação aos bombeiros que realizam combates pontuais.

Finalmente, avaliamos alguns métodos para descontaminar os trajes de combate a incêndio dos bombeiros. Foram avaliadas a fotólise com lâmpada ultravioleta e branca, bem como a adição de um agente oxidante (H_2O_2) para oxidar duas sondas de HPAs. Em relação às fibras, os danos foram verificados por microscopia eletrônica de varredura, microscopia óptica e espectroscopia no infravermelho com transformada de Fourier de reflexão total atenuada. Além disso, foi realizado um teste de resistência ao rasgo (ASTM D2261) no tecido da camada externa da jaqueta. O melhor resultado foi obtido utilizando a fotólise com lâmpada branca (WLP), quando foi possível remover mais de 83% do pireno e 9-metilantraceno previamente depositados. O WLP foi comparado com as técnicas mais utilizadas (lavagem em máquina de lavar e escovação com água e sabão) e apresentou melhores resultados. Com isso, foi possível desenvolver um método de descontaminação simples e barato baseado em fotólise, que seja eficaz na degradação de PAHs, além de manter a integridade das fibras Kevlar® e Nomex®.

Palavras-chave: Hidrocarbonetos policíclicos aromáticos, processos oxidativos avançados, fotólise, resíduos de fogo e vestimentas de combate a incêndio.

INTRODUCTION

CBMDF

The *Corpo de Bombeiros Militares from Distrito Federal* - CBMDF (Military Fire Department of the Federal District) is a military corporation of the Federal District whose mission is to firefighting, civil defense activities, prevention, search and rescue, and public assistance[1].

Article 42, caput, of the Constitution of the Federative Republic of Brazil 1988[2] determines that the members of the military fire brigades are military servants of the States, Territories, and Federal District. For the CBMDF, their attributions are established in the Constitution of the Federative Republic of Brazil[2] and in Federal Law nº. 8,255/91[3], as amended by Law No. 12,086/2009[4], and are:

> "*provide personal and property protection to society and the environment, through actions to prevent, fight and investigate urban and forest fires, rescue, pre-hospital care, and civil defense actions, within the scope of the Federal District.*"

The execution of the corporation's core activities, such as firefighting, rescue, and prevention, are the competencies of the Operational Command, the execution department. Within its structure, there is a division into specialized units, which are:

a) Urban Fire Prevention and Fighting Group;
b) Search and Rescue Group;
c) Pre-Hospital Emergency Care Group;
d) Environmental Protection Group;
e) Civil Protection Group;
f) Operating Aviation Group:
1) 1st Operational Aviation Squadron;
2) 2nd Operational Aviation Squadron.

The Urban Fire Prevention and Fighting Group is responsible for the execution, within the Federal District, of urban fire prevention and fighting activities, described in Decree nº 31,817, of June 21, 2010[5]. The activities of forest fire prevention and combat are the responsibility of the Environmental Protection Group.

Health Risks

The military firefighter profession consists of high-risk activity, having several effects on the physical and mental health of its professionals. Regarding mental issues, Burnout syndrome, depression, post-traumatic stress disorder, anxiety and psychoactive substance abuse are the most described[6,7].

Regarding physical health, lung diseases and lung cancer are the main diseases reported in studies carried out both in firefighters who work in fighting forest fires[8,9] , as in urban fires [10,11]. In a meta-analysis study performed by LeMasters, G. K., *et al.*[12], it was evaluated the risk of cancer in firefighters, identifying an increased likelihood of developing multiple myeloma and a likely association with non-Hodgkin's lymphoma, prostate, and testicular cancer.

In a study carried out with career firefighters from the states of Chicago, Philadelphia and San Francisco, eight types of cancer were evaluated using conditional logistic regression[11]. Male employees who worked between 1950 and 2009 were evaluated. It was possible to correlate a higher mortality with cases of lung cancer and leukemia, with a direct influence on the exposure time and cumulative effect. In a Boston-area study, a study conducted with municipal firefighters, compared with a control group, an increased risk of squamous cell carcinomas of the hypopharynx and larynx was observed[13].

Within the scope of the CBMDF, few studies have been carried out on the subject. Rodrigues, H. A., 2020[14], evaluated the risk of developing melanoma skin cancer in military personnel responsible for firefighting instructions given at the CETOP - *Centro de Treinamento Operacional do Corpo de Bombeiros Militar do Distrito Federal* (Operational Training Center of the Military Fire Department of the Federal District). It was identified that 54% of study participants are at risk for developing melanoma, with 12% at extremely high risk.

Therefore, firefighters have a higher incidence of cancers, resulting from their profession. Because of, after evaluating a series of cancer studies in firefighters and meta-analyses correlating workers' exposure to smoke, IARC (International Agency for Research on Cancer) considered that occupational exposure as a firefighter is classified in Group 2B, that is, possibly carcinogenic to humans[15]. Nowadays, in a meeting that occurred in June/22 at the IARC in Lyon, France, scientists reevaluated the carcinogenicity of occupational exposure as a firefighter. Occupational exposure as a firefighter classified as “carcinogenic to humans” (Group 1) based on “sufficient evidence for cancer in humans” [16]. This assessment will be published in Volume 132 of the IARC Monographs.

Contaminants

During firefighting, the firefighter encounters several chemical compounds present in the smoke that can be called fire residues. Fire residues are a series of gaseous, liquid or solid compounds that are formed during the combustion and pyrolysis process of a material[17]. The chemical composition of the residue depends mainly on the material burned, as well as the conditions under which the burning takes place.

The burning of organic matter is described in equation 1. For example, the complete combustion reaction of the compound methane (CH_4) produces carbon dioxide (CO_2) and water (H_2O). For this reaction to occur, there must be a balance between fuel, oxygen, and temperature (heat), forming the fire triangle (Figure 1). However, in most cases there is no equilibrium in this triangle, and there may be an absence or a greater amount of one or more of the components. Thus, the combustion process that occurs is said to be incomplete, in which extremely reactive free radicals are formed, producing several other compounds and smoke, as shown in equations 2 and 3[18]. In this process, a series of more toxic compounds are formed, as the toxic gas carbon monoxide (CO).

$$CH_4 + O_2 \longrightarrow CO_2 + H_2O \tag{1}$$

$$CH_4 \longrightarrow CH_3\bullet + H\bullet \tag{2}$$

$$H\bullet + O_2 \longrightarrow OH\bullet + O\bullet \tag{3}$$

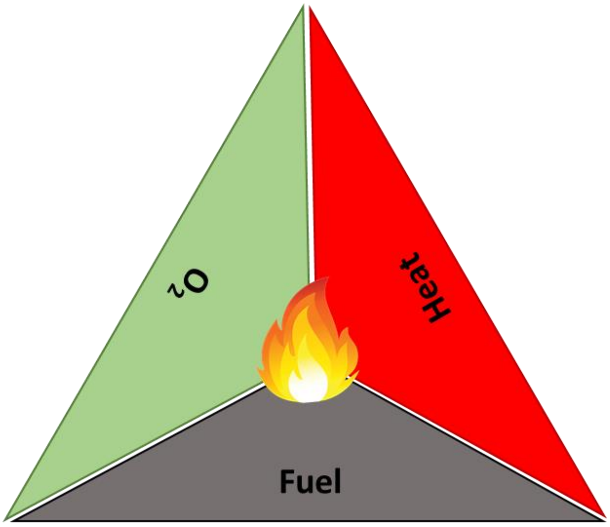


Figure 1. Fire Triangle

In addition to the organic contaminants that are produced during incomplete combustion, the burning of materials containing nitrogen, sulfur and halogens, such as plastics, paintings and woods, can form several other contaminants[17]. The main organic and inorganic compounds found in fire residues will be presented below.

Inorganic Contaminants

The main inorganic compounds produced during a fire are carbon dioxide and carbon monoxide. These compounds have an asphyxiating effect and cause an acute toxic effect, such as: nausea, vomiting, headache, tachycardia, tachypnea and, in more severe cases, convulsions and pulmonary edema[19].

Several gaseous acids are also described as fire residues. Hydrochloric acid (HCl) and hydrocyanic acid (HCN) are formed by burning plastic materials[20]. These also have an asphyxiating effect and can cause death in high concentrations[21]. HCN was the main responsible for the tragedy that occurred in January 2013 at the Kiss nightclub, in Rio Grande do Sul. The burning of foam used as acoustic coating on the ceiling on the walls generated cyanide gas and carbon monoxide, causing the death of at least 234 of the 241 victims of the tragedy[22]. Another acid that can be found is hydrogen sulfide (H_2S), which acts as an irritant to the eyes and nasal passages, causing coughing and difficulty breathing[23].

Nitrogen (NO_2) and sulfur (SO_2) dioxides are also chemicals found in smoke[24]. SO_2 is an irritating agent that causes tiredness, coughing and mucosal damage[21]. On the other hand, NO_2, when inhaled, can cause lung damage even in small concentrations, so that the severity of the damage is dose-dependent[25].

Ammonia (NH_3), a purging gas with a characteristic odor, has an irritating effect and high exposures can cause lung damage and pneumonia[20,21]. The compound is found as fire residue from nitrogen-containing materials, along with NO_2[26].

Heavy metals such as cadmium, antimony, and lead are present in ash and are dispersed into the air during fires. Lead (Pb), a toxic metal that accumulates in the body, can cause several biological, neurological, hematological and cardiovascular changes, among others[27]. Cadmium (Cd) causes several effects, and an acute exposure can cause fever, muscle pain and lung damage[28]. Antimony (Sb) is related to hematological and histological alterations in the thyroid, in addition to respiratory and gastrointestinal effects[29].

In addition to the inorganic compounds described above, the incomplete combustion process produces an aerosol of solid carbon particles, called particulate matter. According to the United States Environmental Protection Agency (USEPA)[30], particles larger than 2.5 and smaller than 10 micrometers are considered coarse inhalable particles, while particles smaller than 2.5 micrometers ($PM_{2.5}$) are considered fine particles. Fine particles are the most harmful to health, reaching the lungs and heart. Chronic exposure to $PM_{2,5}$ is related to an increase in respiratory and lung diseases, as well as an increase in cancer and higher mortality in the general population[9] and in the elderly[31].

Organic Contaminants

Several organic compounds are produced by burning materials. With the introduction of synthetic materials, substances considered more toxic are found in residential and industrial fire residues when compared to forest fires[32–34]. The main compounds described are: volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs)[23,35].

According to USEPA[36], VOCs consist of organic compounds that can evaporate under normal atmospheric conditions of temperature and pressure, that is, that have a boiling point (BP) lower than or equal to 250ºC, with an atmospheric pressure of 101.3 kPa. The World Health Organization (WHO)[37] has classified VOCs into three categories: very volatile organic compounds (VVOCs), volatile organic compounds (VOCs) and semi-volatile organic compounds (SVOCs). A number of VOCs are described as fire residues, often found in concentrations above those regulated by monitoring bodies[38]. Compounds of lower chemical structure, even heavier compounds are found, as exemplified in Table 1.

Table 1. Classification of VOCs and examples of compounds described with fire residues.

Nomenclature	Characteristics	Compounds
VVOCs	Compounds that have BP < 0 to 50°C - 100°C	Acetone, chloromethane, bromomethane
VOCs	Compounds that have BP in the range of 50ºC to 260ºC	Formaldehyde, toluene, xylene, styrene

SVOCs	Compounds that have BP in the range of 240-260 to 380-400	PCBs, PCDFs, PCDDs and phthalates

Source: Adapted from de USEPA[36].

Despite being more commonly reported as environmental and occupational contaminations relevant to gas stations, BTEX (Benzene, Toluene, Ethylbenzene and Xylene) are also considered as fire residues[24]. BTEX is a set of pollutants that includes the VOCs benzene, toluene, ethylbenzene and xylene, compounds that have a benzene ring in their chemical structure, Figure 2. As described by Alharbi, B. H., *et al.*[26] and Austin, C. C., *et al.* [38] benzene is one of the compounds with the highest concentration in fire smoke. Because they are fat-soluble and act as central nervous system depressants, BTEX can cause deleterious effects even at low concentrations[39].

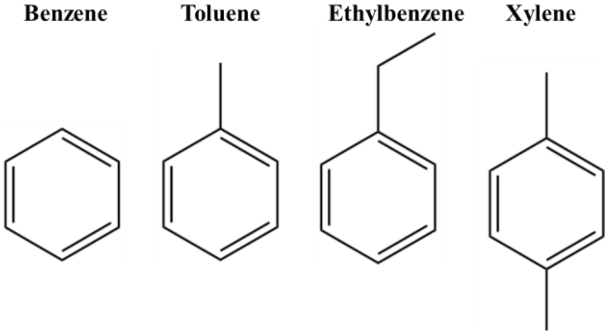


Figure 2. BTEX structure: benzene, toluene, ethylbenzene and xylene.

PCBs (polychlorinated biphenyls) are organochlorine compounds that present in their structure benzene rings, in their basic structure, as shown in Figure 3a. One of the sources of this material is due to the use of flame retardant additives and additives in the formulation of plasticizers[40]. Contact with these compounds causes several harm, having genotoxic and teratogenic effects and is related to the increase in cases of liver and gallbladder cancer[41].

Polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzodioxins (PCDDs) are organochlorine compounds with chemical structure described in Figure 3b and 3c, which can bioaccumulate within trophic chains. These compounds have the ability to interact with cytochromes in the liver, causing several toxic effects, being considered carcinogenic and teratogenic[42]. These compounds are found in post-fire scenes and are deposited in firefighters' PPE (personal protective equipment). PCDD/F were found in Taiwan/China firefighters' helmets after fighting fires at levels above those found in the local population[43].

Phthalates are esters (Figure 3d) formed by the reaction of phthalic acid (carboxylic acid) with an alcohol and are typically used as additives to make plastic more malleable[44]. In a study carried out by Fabian *et al.*[21] the compound bis(2-ethylhexylphthalate) (BEPH) showed the highest concentration in firefighter gloves and hoods used for 2, 4, 6 and 8 weeks. BEFT is classified in group 2B by IARC[45] and is considered possibly carcinogenic to humans.

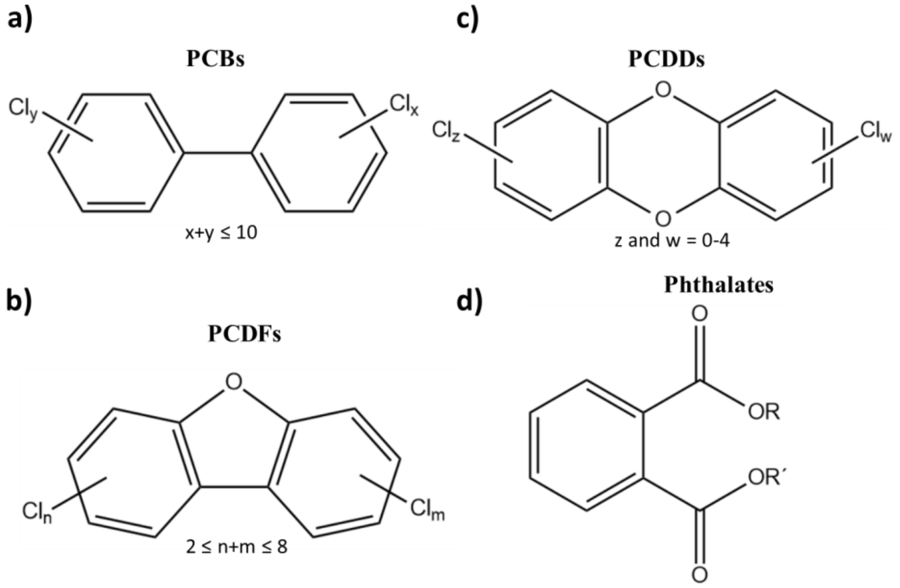


Figure 3. Generic structures for the compounds: PCBs, PCDFs, PCDDs and phthalates.

Many of the compounds described above are classified as persistent organic pollutants (POPs), that is, they are organic molecules that have high toxicity and are recalcitrant in the environment, difficult to degrade, and can be bioaccumulated and biomagnified.

In addition to VOCs, another class of recalcitrant pollutants is polycyclic aromatic hydrocarbons (PAHs). Such compounds have high toxicity and will be the subject of the present study, being discussed in more depth in the next topic.

Polycyclic Aromatic Hydrocarbons (PAHs)

Among the compounds described as organic residues from fire, one of the most studied classes in the literature is the Polycyclic Aromatic Hydrocarbons. PAHs consist of a class of organic compounds with more than 100 substances that present in their structure two or more aromatic rings condensed in different ways, as shown in Figure 4.

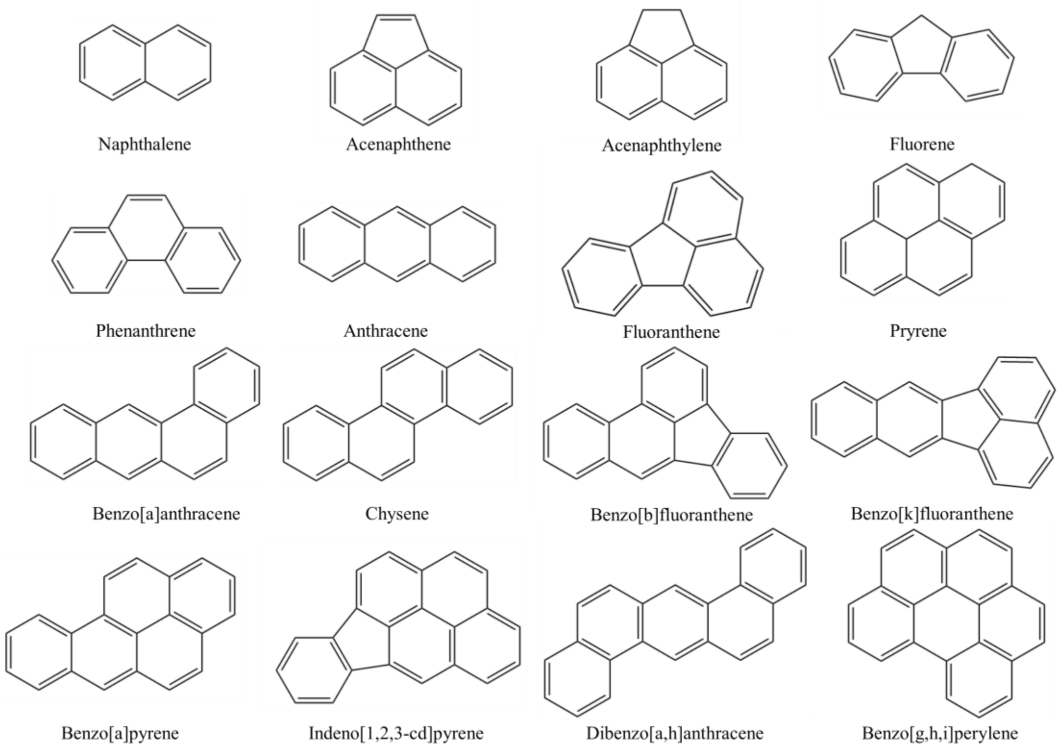


Figure 4. Sixteen priority PAHs in environmental studies according to the USEPA[46].

The main sources of these materials can be divided into three categories: pyrogenic, petrogenic and biological[46–48]. Pyrogenic processes are those that involve incomplete combustion, at low temperatures and with low concentrations of oxygen. The petrogenic processes involve maturation of crude oil and derivatives, in addition to their use, storage and transport. Finally, biological processes are those in which PAHs are produced by fungi or plants, involved in the degradation of organic matter such as leaves and wood[49]. Although these pollutants are found naturally in the environment, the vast majority are produced in anthropogenic processes (Figure 5)[46,50].

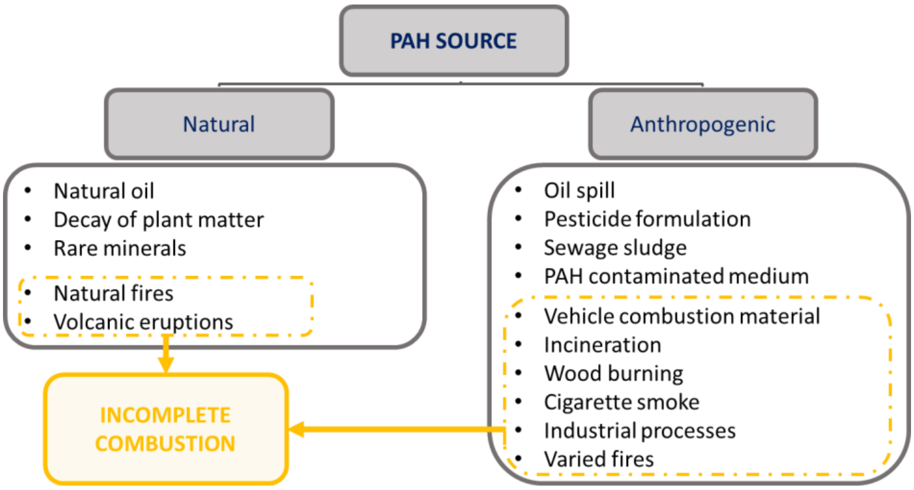
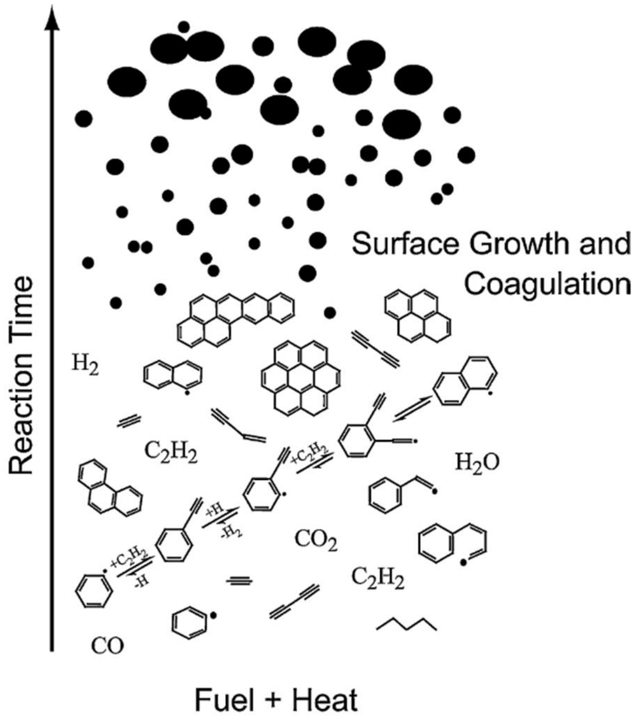


Figure 5. Main sources of PAH[47,48,51].

During a fire, PAHs are formed through radical reactions from compounds of lower molecular weight, as described in Figure 6. The first aromatic ring is formed from the fragmentation of the fuel resulting from the combustion process. Then there is the reaction of this ring with smaller molecules promoting the growth of PAH[52].



Source: Richter, H. e Howard, J. B., C. M., 2000.

Figure 6. Formation of PAHs during a fire [53].

Three factors influence the formation of PAHs: fuel, amount of O_2 and temperature. In fires with benzene-derived fuels, there is a 100 times greater production of PAHs than in burning with saturated fuels[53].Besides, in an oxygen-poor atmosphere, there is a greater formation of PAH[54], while in O_2-rich burns, there is a favor for the total burning of the material, forming CO_2 and H_2O. Finally, in low temperature burning forms PAHs substituted with alkyl groups, a common fact in forest fires[55]. At high temperatures, compounds without substituents are formed[56].

Toxicity

The concern about the presence of these compounds in fire residues is due to the fact that many PAHs are considered carcinogenic, mutagenic and teratogenic[57]. These characteristics give these contaminants inclusion in most environmental and human health monitoring programs in different countries around the world, such as WHO 1983[58] and USEPA 1986[59]. The 16 priority PAHs according to USEPA (Figure 4) are primarily responsible for problems related to environmental and health issues[48].

For humans, the route of exposure may occur through inhalation, ingestion, or the dermal route. Toxicity is directly related to molecular size, in addition to its recalcitrant effect on the environment. According to IARC 2014[60], the compound Benzo(a)pyrene belongs to group I, is classified as carcinogenic to humans, being the most toxic of the PAHs. However, other PAHs are known for their possible toxicity to humans or animals. Of the 16 major PAHs, 11 are considered photomutagenic, that is, they produce mutagenic compounds when irradiated with UV lamp, 7 are considered carcinogenic and 8 are mutagenic (Table 2)[61].

Table 2. Toxicity of the 16 major PAHs [61].

Compound	Photomutagenicity	Carcinogenicity	Mutagenicity
Acenaphthene	+	0	-
Acenaphthylene	+	I	-
Anthracene	++	0	-
Benzo(a)anthracene	++	++	+
Benzo(a)pyrene	++	++	+
Benzo(b)fluoranthene	-	++	+
Benzo(ghi)perylene	++	I	-
Benzo(k)fluoranthene	+	++	+
Chrysene	+	+	+
Dibenzo(a,h)anthracene	-	++	+
Phenanthrene	-	I	-
Fluoranthene	-	0	+
Fluorene	+	I	-
Indeno(1,2,3-cd)pyrene	++	++	+
Naphthalene	-	I	-
Pyrene	++	0	-

Caption:
+ (photomutagenic), ++ (very photomutagenic)
0 (no evidence of carcinogenicity), I (inadequate evidence for evaluation), + (limited evidence of carcinogenicity in animals), ++ (sufficient evidence of carcinogenicity in animal experiments)
+ (mutagenic), - (non-mutagenic)

Source: WHO; IARC, 2010.

In the specific case of firefighters, the main route of exposure is inhalation[62]. One way to reduce this contamination is using self-contained breathing apparatus (SCBA). Another exposure route for firefighters is through the dermal route, which can occur mainly through the deposition of contaminants directly on the skin, as well as through cross-contamination, contact with a contaminated surface. Several PAHs were found in personal protective equipment for firefighting and direct contact with this contaminated PPE can become an important route of contamination.

Considering the formation of these compounds in fires and their relationship with the occupational health of firefighters, three scenarios were evaluated in this work:

a) Brazilian firefighters working practices regarding their health (chapter 1);
b) The presence of PAHs in firefighter PPE after fire training exercise (chapter 2);
c) Development of a chemical decontamination method of firefighting protective clothing impregnated with PAHs (chapter 3).

CHAPTER 1

BRAZILIAN FIREFIGHTERS WORKING PRACTICES REGARDING THEIR HEALTH

1. Theoretical reference

In a study performed by Daniels *et al.*[63], U.S. firefighters have a 9% higher risk of being diagnosed with cancer and a 14.9% higher risk of dying from cancer than the general U.S. population. One way to reduce the statistic is the correct use of firefighters' PPE, and an effective PPE cleaning, preventing avoid direct contact of carcinogenic substances with firefighters' skin[64].

Firefighter organizational culture has traditionally associated dirty gear to a symbol of hard work[65]. A recent British report[66] showed that this "badge of honor attitude" still prevails among firefighters in the UK. The authors define the "badge of honor attitude" as pride in having soiled PPE to give the impression of their being hardworking. On the other hand, the proper use and cleaning of this individual protective equipment (PPE) can considerably reduce the risk of cancer among workers. There has been a growing awareness in this regard[67,68]. The correct use of PPE can prevent direct contact of toxic substances with the skin of firefighters; effective cleaning of their PPE can remove most of the carcinogenic substances[64]. Consequently, it is important to assess firefighters' awareness of risks, risk reduction procedures and, ultimately, whether there has been an ongoing change in the culture of caring for PPE. In fact, some studies have already indicated a change in the organizational culture of firefighters, whether this change is dependent on the region, and whether or not there are internal norms and peculiarities among the groups studied[69].

The studies of Hwang *et al.*,[70] evaluated variables related to PPE use, storage and cleaning practices in Northwestern Kentucky (USA). The research shed light on some of these issues. For instance, volunteer firefighters tended to use older turnout gear than career firefighters, who have their gear replaced more frequently; 21% of career firefighters' and 53% of volunteer's store their turnout gear in a personal vehicle, which is not recommend by the National Fire Protection Association (NFPA); and the advanced PPE cleaning procedures recommended by (NFPA) is not followed in small rural fire departments. On the other hand, another research carried out by Macy et al.,[68] with rural firefighters from Kentucky (USA), revealed that most of the interviewees were compliant with NFPA Standards, cleaning their gear as needed, storing gear in the fire station and retiring gear within 10 years of the manufactured date. Also, most of the participants were aware of job-related exposures risks and felt susceptible to cancer and respiratory illness.

In the literature on the subject, most studies have been focused on actual rates of firefighter cancer and the mechanisms of exposure [14,62,63,71]; few have focused on firefighter awareness of the risk of cancer in their profession or the adoption of good occupational practices[72]. In the case of Brazil, the number of works are even smaller, and no studies focused firefighter attitudes and norms about cancer and risk reduction resulting from occupational practices were found.[72]

Considering that, we develop a form to map some firefighters' habits regarding these and the impact of firefighter habits on their health (considering occupational risk of developing cancer). The study focused on the issues of PPE cleaning and storage, as well as firefighter cancer risk awareness. It was carried out with firefighters from the Brazilian Distrito Federal (CBMDF) and the state of Pernambuco (CBMPE) fire departments.

2. Objectives

This research seeks to analyze the impact of firefighter attitudes and behaviors on their health. Hence, a study focused on issues as PPE cleaning and storing and firefighter cancer risk awareness was carried out with firefighters from Distrito Federal (CBMDF) and Pernambuco (CBMPE) fire departments.

The specific objectives of the work consist of developing an instrument for the evaluation of the firefighter attitudes and behaviors, based on previous works described in the literature.

3. Materials and Methods

To investigate firefighters' routines and habits, focused on PPE cleaning and storage culture of use and washing of PPE by firefighters, a form containing twenty-eight questions was prepared and applied to the *Corpo de Bombeiros Militares do Distrito Federal* (CBMDF) and *de Pernambuco* (CBMPE) - (Federal District and Pernambuco Military Fire Department). The same form was applied in both regions and can be seen in the annex of this work.

The main objectives of this questionnaire were to determine the awareness of firefighters about the risks of exposure to fire residues and about PPE cleaning routines.

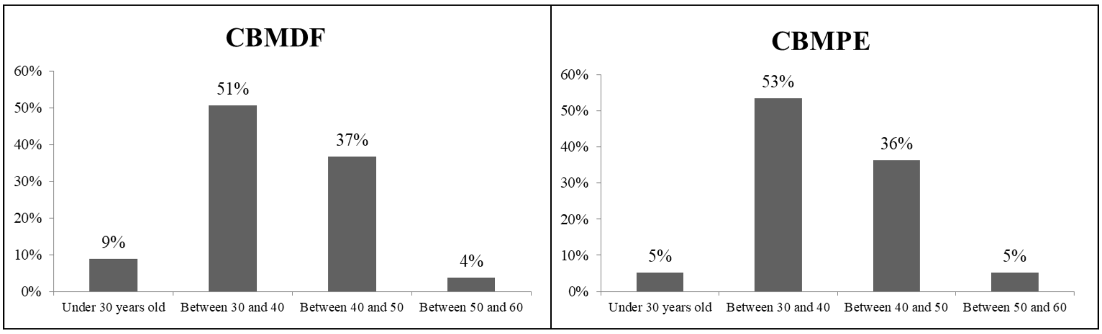
The form design contained 28 questions regarding the profile of the respondent, with questions related to the washing and storage habits of PPE used in firefighting, as well as personal information, such as age, length of service, grouping, graduation, among others. These were followed by a series of statements to be graded on the 5-point Likert scale, with the options strongly agree, agree, neutral, disagree and strongly disagree. The guidelines provided by each institution and the perceptions of each firefighter on issues related to the research topic were also evaluated. The Google Forms plataform was used to collect the answers and as advertised in the firefighters' WhatsApp groups and by direct e-mail. All participants were kept confidential, and their answers were not provided to their superior colleagues.

The research was carried out in the state of Pernambuco and in the Federal District, considering the interest in the subject, demonstrated through contacts with Major Wilson Paulo da Silva (CBMPE) and Captain Bruno Marcelino de Almeida Nunes (CBMDF).

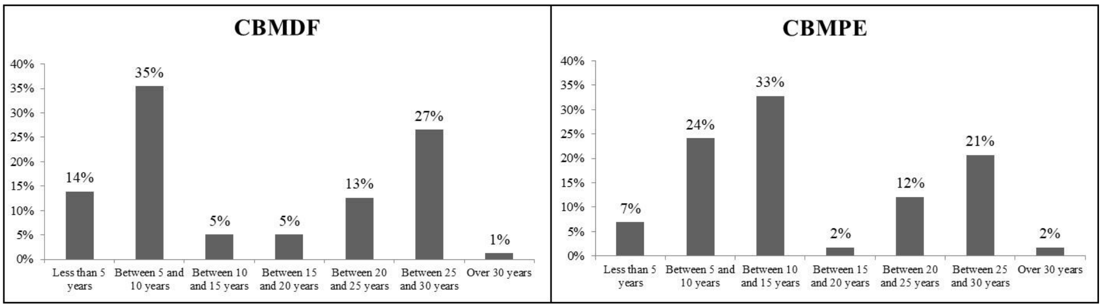
4. Results and Discussion

To assess the firefighters' routines and habits, a Google Form with 28 questions was developed and applied to 137 firefighters from two fire corporations in Brazil participated in this research. Those surveyed worked in two corporations: *Corpo de Bombeiros Militar do Distrito Federal* (CBMDF) (79 answers) and *Corpo de Bombeiros Militar de Pernambuco* (CBMPE) (58 answers). In Pernambuco, there are about 2500 military firefighters, therefore a sample of 58 respondents corresponds to, within 90% of confidence, about 10% of error (10.6%). In the Federal District, the contingent of military firefighters is close to 6000, so a sample of 79 respondents corresponds, with 90% confidence, also to an error close to 10% (9.2%)

First of all, we looked for better know the profile of firefighters. Regarding age, most of the participants are in the 30-40 years group (50%, 40 responses), followed by the 40-50 years group and then, the two extremes ages (under 30 and up to 60), as shown in Graph 1. Both corporation has shown a similar age profile. Regarding time of service, most participants have 5 to 10 years of service, as shown in Graph 2, however a wide distribution is observed in both corporations.

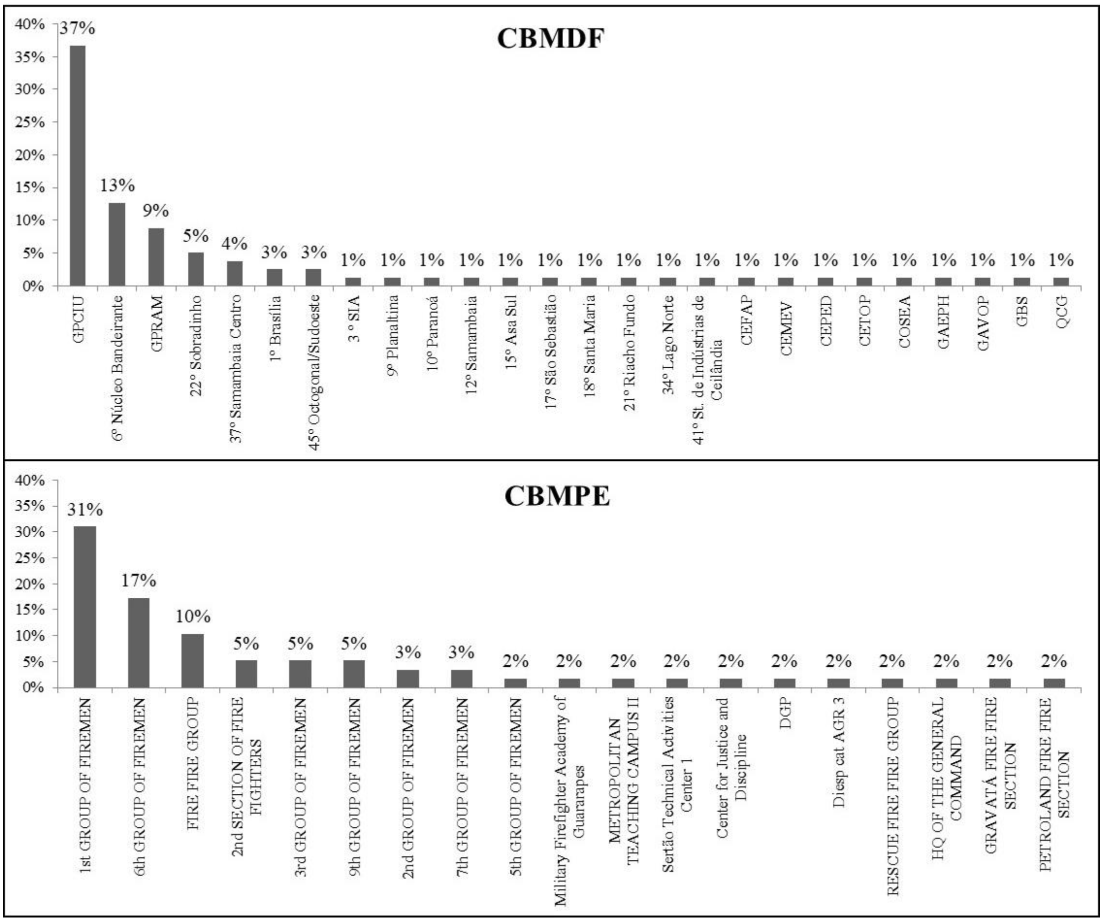


Graph 1. Age of military firefighters participating in the research.

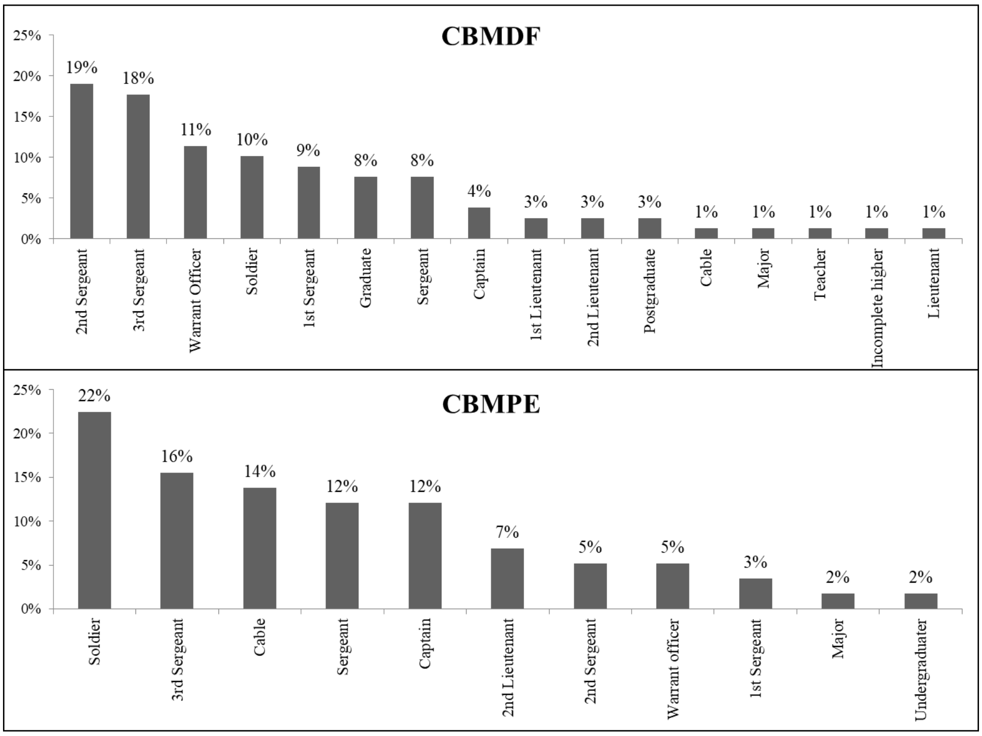


Graph 2. Service time of the military firefighters participating in the research.

In addition, it was evaluated to which Military Firefighter Group the participant belonged, their rank and function, and the responses are shown in the 3, 4 and 5 Graphs, respectively,

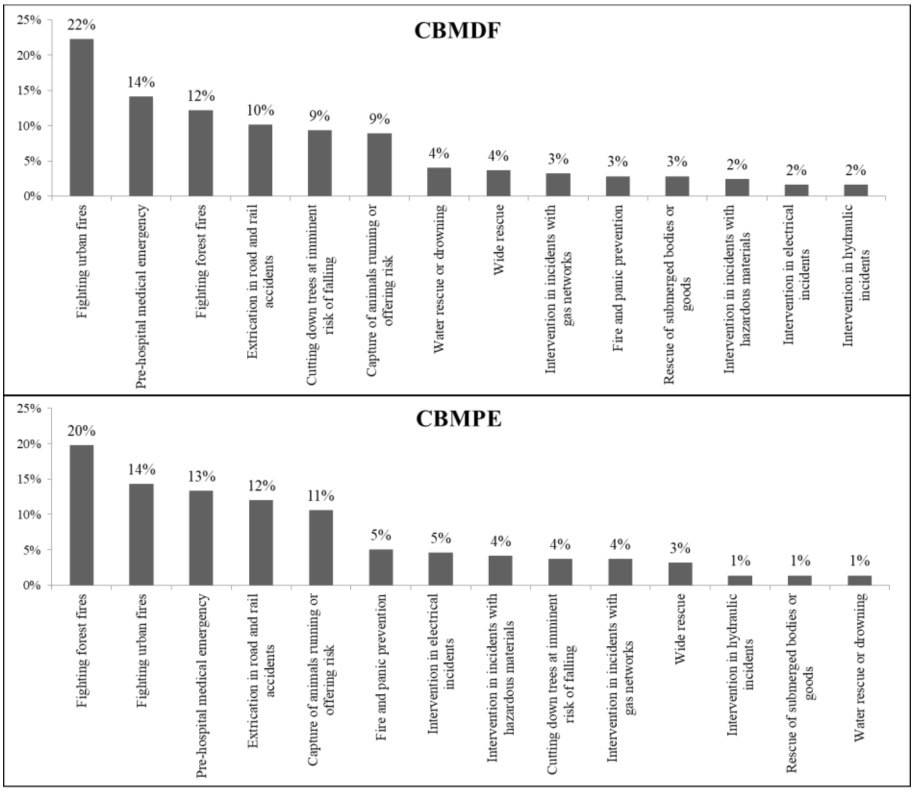


Graph 3. Military Firefighter Group that the research participants belong to.



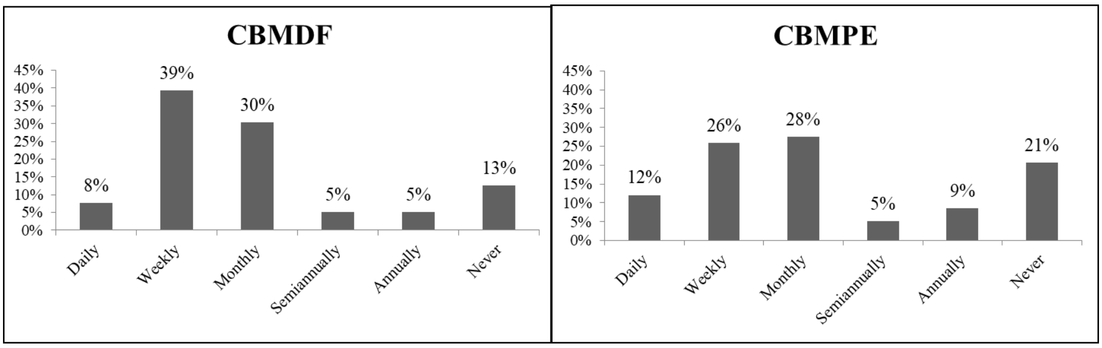
Graph 4. Graduation of research participants.

Regarding related activities during the exercise of the function, most related the contact to urban fires (20-22%), followed by pre-hospital medical emergency (13-14%) and fighting forest fires (12-13%). Considering the answers, most of the services provided (36 and 34%) are related to firefighting. Other activities are also carried out, as described in Graph 6.



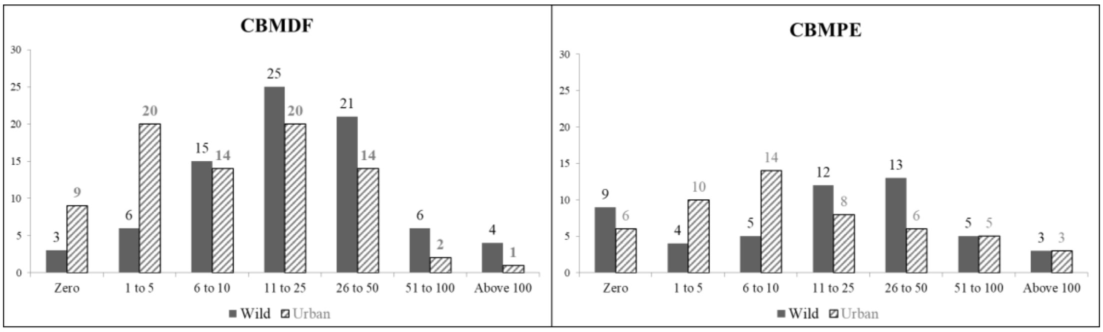
Graph 5. Types of services that are most performed by firefighters.

Regarding contact with hazardous chemicals (eg flammable liquids, oxidizing substances, toxic gases, toxic substances), Graph 6, most participants reported that contact occurs weekly (39% and 26%) or monthly (30% and 28%). With this, it was possible to identify an important portion of the sample which keep contact with hazardous substances, what could lead to long term exposure health problems. It is noteworthy that in the CBMPE there is a high percentage of people who claim never to have contact with hazardous products (21%), especially because 34% of respondents claim to work in firefighting, incidents with gas or toxic products. On the other hand, 52% of CBMPE respondents stated that they mostly perform activities not related to fire or toxic products - so it is possible that 21% actually have no or little contact with toxic products.



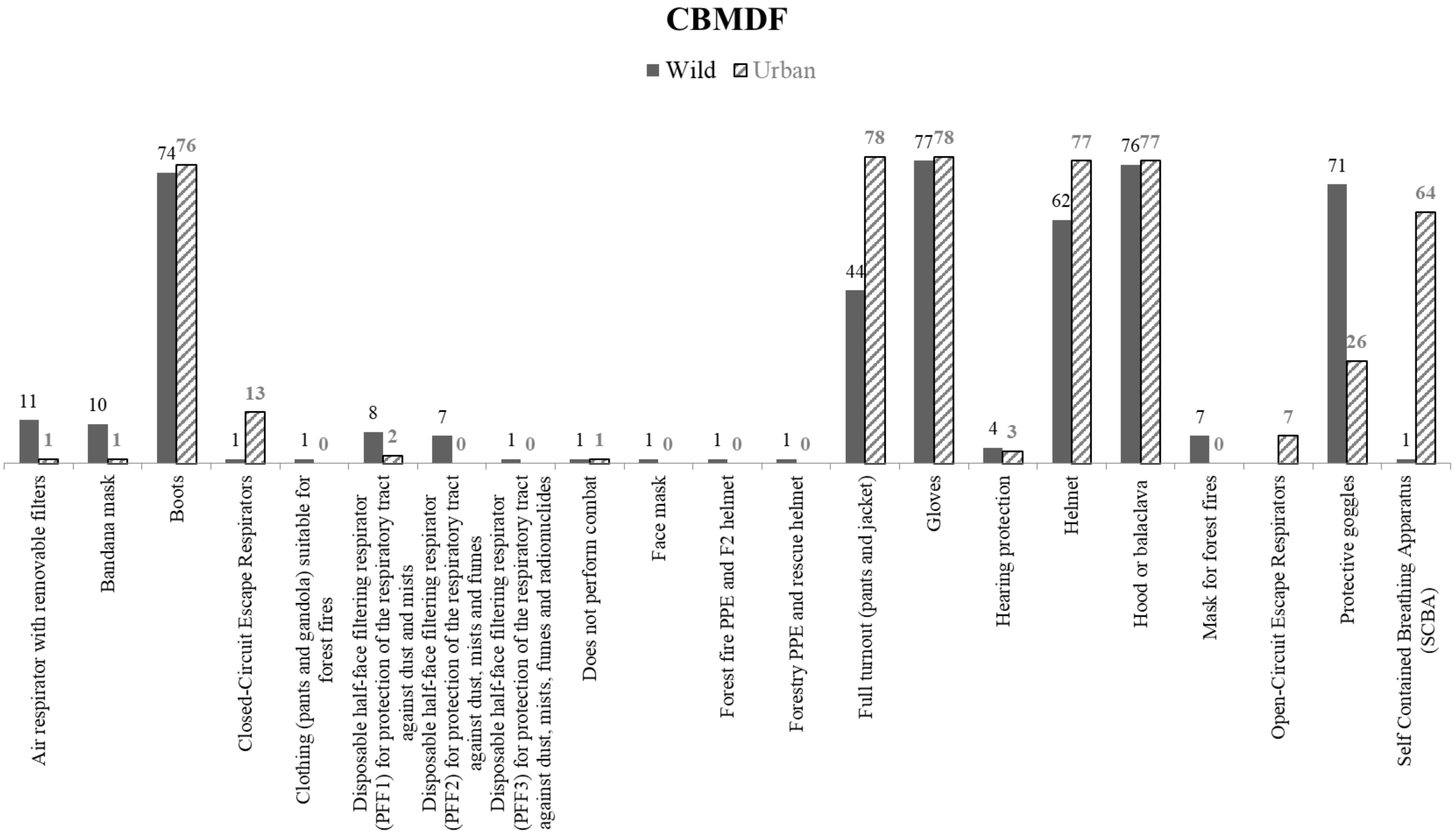
Graph 6. Frequency that research participants meet hazardous chemicals during their work.

Considering that the main activity performed by firefighters is related to firefighting, participants were asked about the number of attendances for forest fires and urban fires (Graph 7) performed annually. The largest number of services provided is to combat forest fires, both for CBMDF and CBMPE.

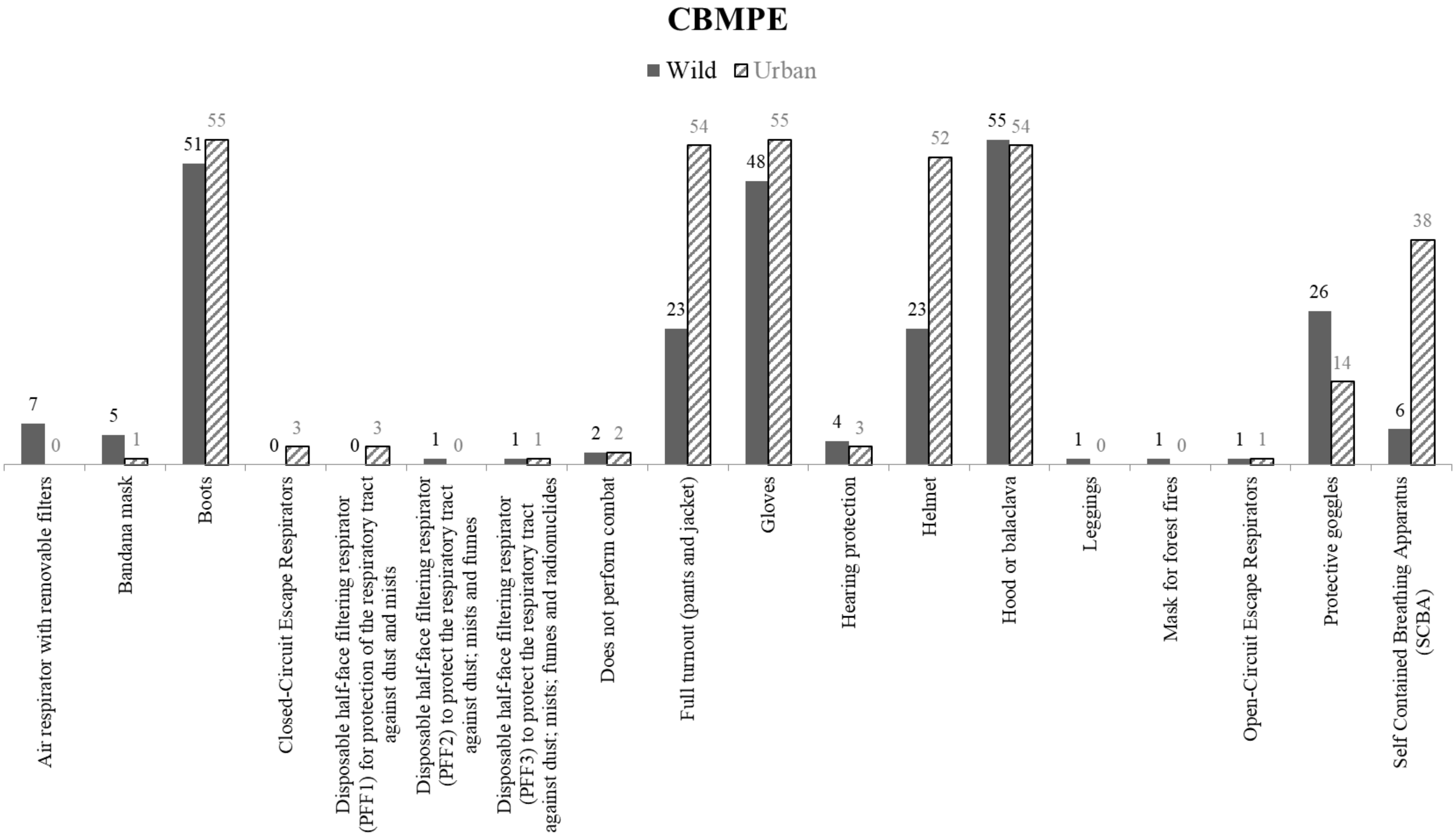


Graph 7. Number of forest and urban firefighting carried out annually by the research participants.

In the following questions on the form, questions related to the use of PPE, storage and hygiene were asked. Initially, firefighters were asked about the equipment used to fight forest and urban fires (Graphs 8 and 9). In the case of urban fires, an appropriate mask with breathing air cylinders, self-contained open or closed-circuit mask air adduction respirator is used. Such equipment provides greater protection to users as they prevent contact with contaminants. In the case of forest fires, air respirators with removable filters, disposable half-face filter respirators (PFF1/PFF2/PFF3) are used. Such equipment does not provide complete protection against waste fire compounds. Regarding the use of full approach clothing, only 44 and 23 of firefighters use it in cases of forest fires. This fact, together with the use of detachable masks, may be related to a higher risk of developing cancer in this population.

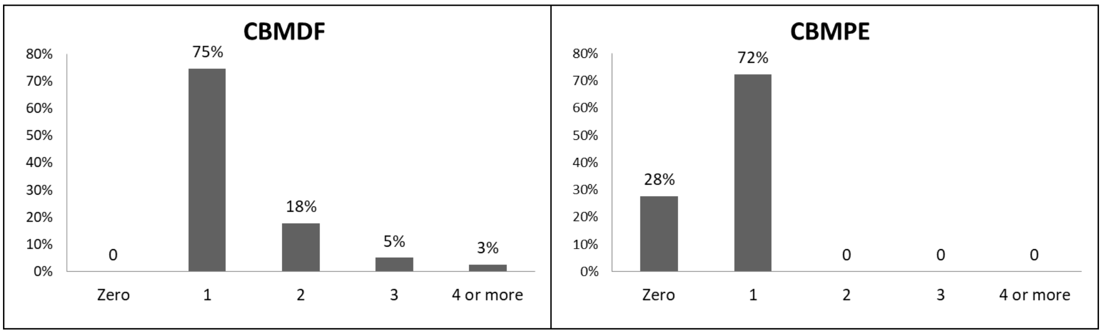


Graph 8. PPE used in fighting urban and forest fires by participants from CBMDF.



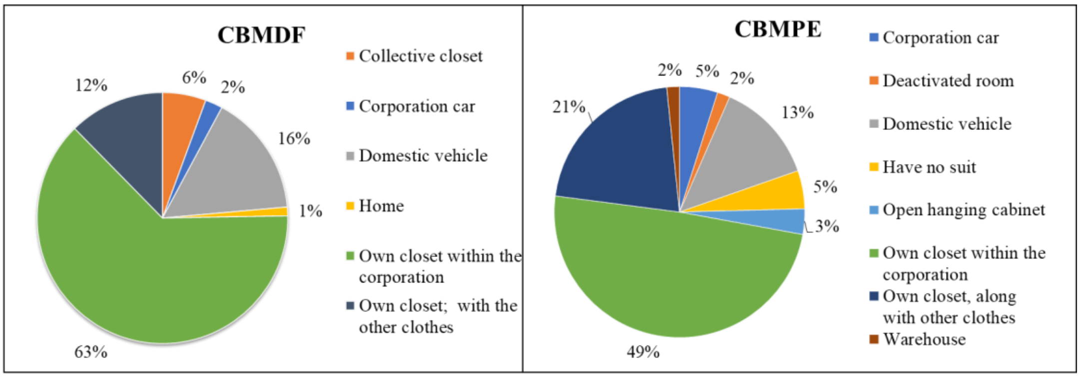
Graph 9. PPE used in fighting urban and forest fires by participants from CBMPE.

To assess what would be a compromise between the number of washes and the routine of firefighters, it is important to know how many suits each firefighter has (and whether or not they could rotate between them). Graph 10 shows that 75% of CBMDF firefighters have only one suit and only 18% have more than one suit, while 28% of firefighters of CBMPE do not have any suit and 72% have only one. It is also noteworthy that, of this percentage of firefighters in Pernambuco who do not have a fire suit because only 7% said to not carry out any type of firefighting. In other words, 21% of these soldiers regularly fight fires and still do not have their own attire. This information leads us to believe that this percentage of the sample carries out firefighting with collective suits or eventually without the appropriate suits. In addition, the absence of personal attire may reflect the lack of regular and controlled washing, if collective attire is used. A greater number of suits would be important because it would allow the firefighter to wash the PFPC (proximity firefighting protective clothing) more frequently.



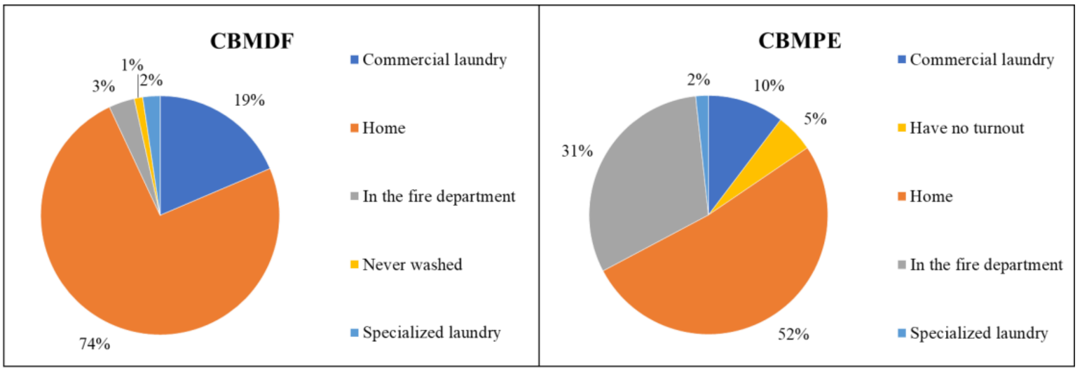
Graph 10. Number of turnout gear that the military firefighters participating in the research have.

Another issue that may be related to increased cancer risk in firefighters is the storage location of the firefighting suit (Graph 11). Most suits are stored in their own locker (63% CBMDF and 49% CBMPE), inside the corporation. This is most adequate way to store suits since it avoids cross-contamination with other personal items. On the other hand, a considerable portion of the participants store the costumes in their vehicles and in a personal closet along with the other clothes. This inadequate storage favors greater contact, both by firefighters and family members, and may be a contributing factor to contamination and increasing the risk of developing cancer.



Graph 11. Storage locations for research participants' firefighting turnout gear.

Another important issue is related to the cleaning routine of personal protective clothing. The firefighters were asked where they cleaned their suits (Graph 12). Most of participants cleaned their suits at home (63-49%), which would be contraindicated because it increases the risk of cross-contamination not only for the firefighter his/herself but also for other family members and/or residents. About 19-10% used commercial laundry shops, which could be a greater problem due to the risk of contaminating other clients' clothes. Mayer *et al.*[74] demonstrated the cross-contamination risk when cleaning firefighter gear and different clothes in the same laundry cycle. They laundered firefighters' hoods (used in firefighting) and new hoods (never used) in the same laundry cycle. The result was that toxic compounds were detected in the unused hoods. Although washing at home was more frequent in both cases, in Pernambuco, washing at the fire department was prevalent (31% versus 3% in the CBMDF). This variation reflects regional heterogeneity and was expected. Nevertheless, both corporations are still far from an ideal scenario, and even in the CBMPE, the percentage of suit cleaning at fire department was quite low.

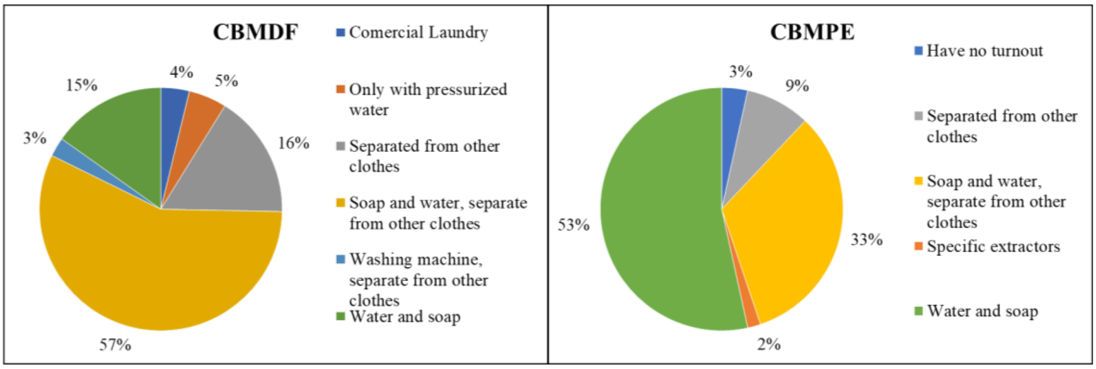


Graph 12. Locations for cleaning the firefighting turnout gear of research participants.

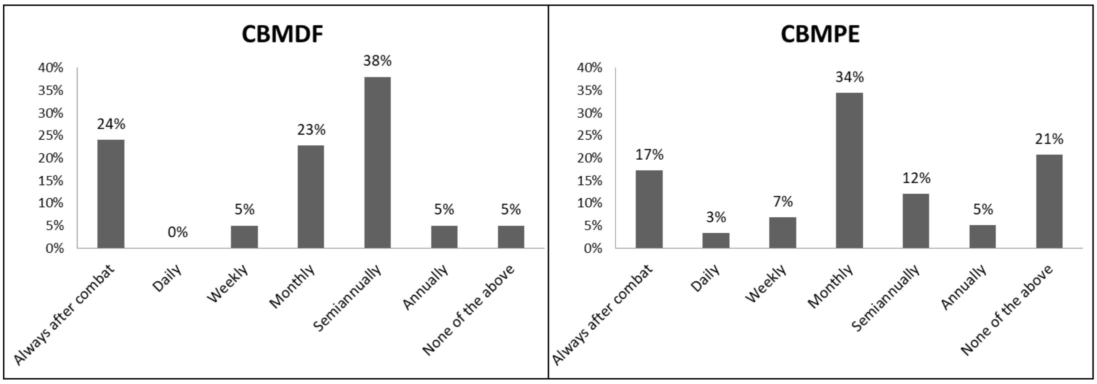
Following this, the cleaning methods and frequency were questioned. Results are shown in Graphs 13 and 14. Most of participants said that they used soap and water to clean their suits. Besides conventional laundering, some firefighters decontaminated their clothing at the combat scene with pressurized water and neutral soap. This cleaning procedure was confirmed in an informal conversation with some firefighters. Although most respondents indicated that they washed their protective clothing with soap and water, some respondents indicated using of only water (5% - DF). Washing with soap and water (or detergent) is considered the most effective way to remove PAHs and other contaminants. Keir *et al.*[67] compared the removal of PAH from the skin with water and soap or use commercial wipes after fighting a fire. Only washing with soap and water was effective for removing most of the PAH, although the results were not as good for removing naphthalene. Fent *et al.*[64] compared three types of cleaning methods: wet-soap method, which had 85% of PAH reduction; dry-brush method, with 23% of PAH reducti\on and air-based decontamination method, removing only 2% of the PAH present.

In addition to the correct cleaning of the PFPC, cleaning frequently is also a relevant factor (Graph 14). NFPA[75] recommends that turnout should be cleaned just after being used to reduce risk of contamination by handling or storage. However, it might be incompatible with firefighters' routine since wet suits cannot be used and most firefighters only have one suit. The washing always after the fight is carried out by 24% of the firefighters of the CBMDF and by 17% of the CBMPE. Most participants carry out the washing monthly and semi-annually. It is noteworthy that 5% from DF and 21% from PE of the participants had answered "none of the previous options", which implied a very low and worrying frequency of cleaning the clothes. Of course, the hypothesis cannot be ruled out that, at least a part of this percentage, did not act or were only occasionally active in situations that required cleaning of the suit. Controversially, in informal conversation with the participants, many reported avoiding washing their clothes for a long period of time, this is due to the fact that the fabrics can be worn out and lose their properties[76–78].

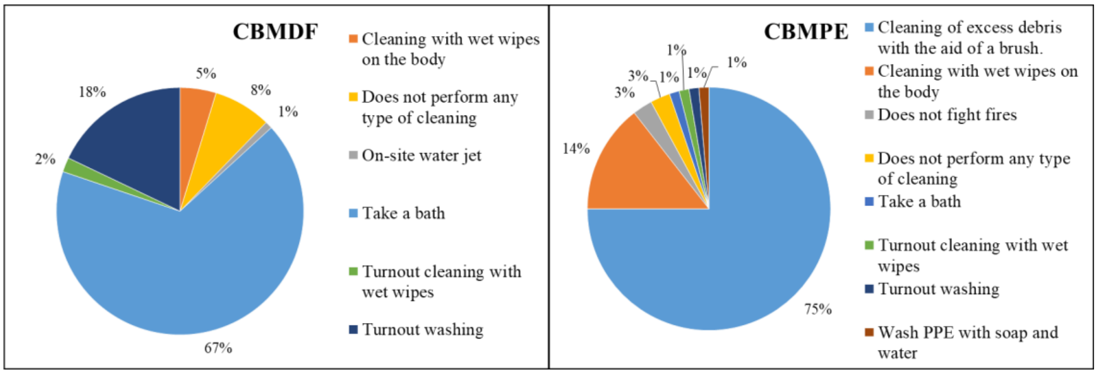
When carrying out the unequipment process, the firefighter can be indirectly contaminated. For this reason, it is important to carry out some type of cleaning after fighting a fire (Graph 15). Most participants take a shower, however, other techniques are also performed, such as the use of a water jet. An important fact is that 8% of the participants in the DF do not perform any type of decontamination, as shown in Graph16. This increases the risk of developing cancer due to contact with contaminants and demonstrates that firefighters need to raise awareness.



Graph 13. Firefighting turnout gear cleaning method performed by the research participants.



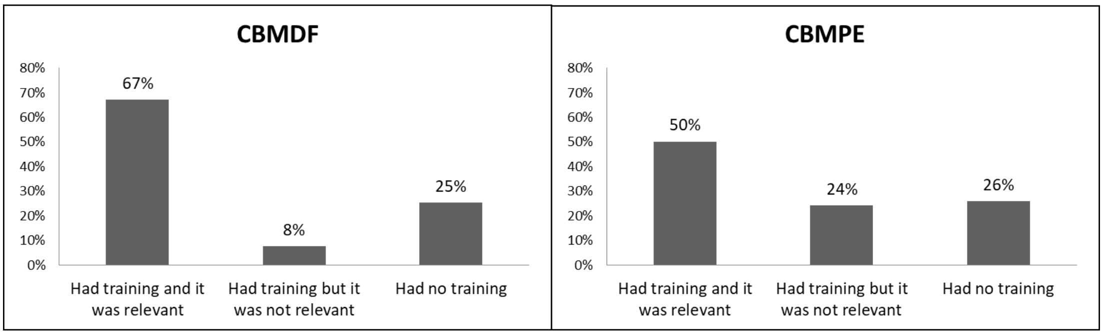
Graph 14. Frequency in which firefighting turnout gear are washed.



Graph 15. Firefighter sanitation methods after fighting a fire by research participants.

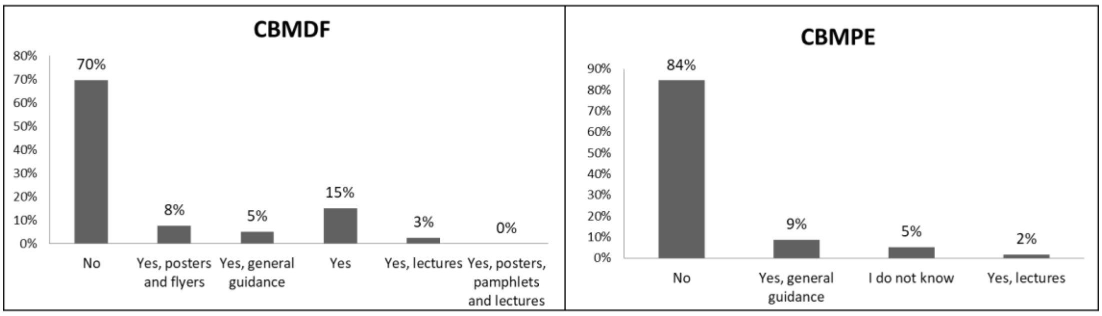
The second part of this work was focused on mapping the participants' level of awareness about the risk of developing cancer, the relationship between the development of cancer and some attitudes after firefighting. Graphs 16-18 demonstrate training and awareness of the use of PPE within the battalion, group, and State, respectively.

Most firefighters in the survey received training about relevance of using PPE and consider it relevant (67% CBMDF and 50% CBMPE). Upon joining the force, all firefighters carry out a series of training and instructions, a fact that is related to the high number of the response. A considerable percentual of respondents claimed had received no training. When analyzing the responses individually, 91% of the participants who marked this option are over 30 years old. So two hypothesis come out. Firstly, training about awareness of the use of PPE were recently introduced in corporations so that older firefighters did not participate in such activities (after 2020). Secondly, the respondents did not consider the initial training as they have been in the service for some time. Periodic training is important to remember and emphasize the need for some practices, as well as to update some procedures.

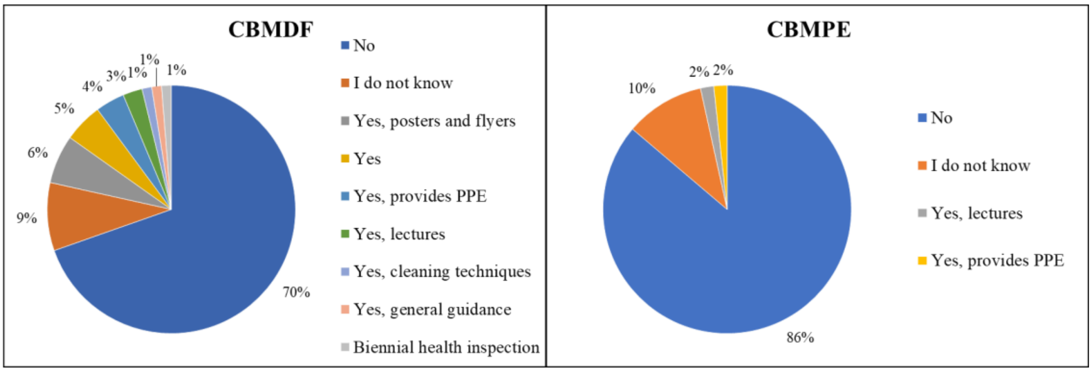


Graph 16. Promotion and significance of training carried out within the battalion to raise awareness of the use of PPE by research participants.

Finally, firefighters were asked about receiving guidance for reducing cancer risk by state. Most answers point to no guidance provided (70% CBMDF and 86% CBMPE). This demonstrates that there is still no institutional politics concerning cancer preventions and decreasing risk of contamination of firefighters with carcinogenic products. During an informal conversation with CBMDF firefighters, it was reported that a change in corporate culture is underway and such activities are being planned and carried out.

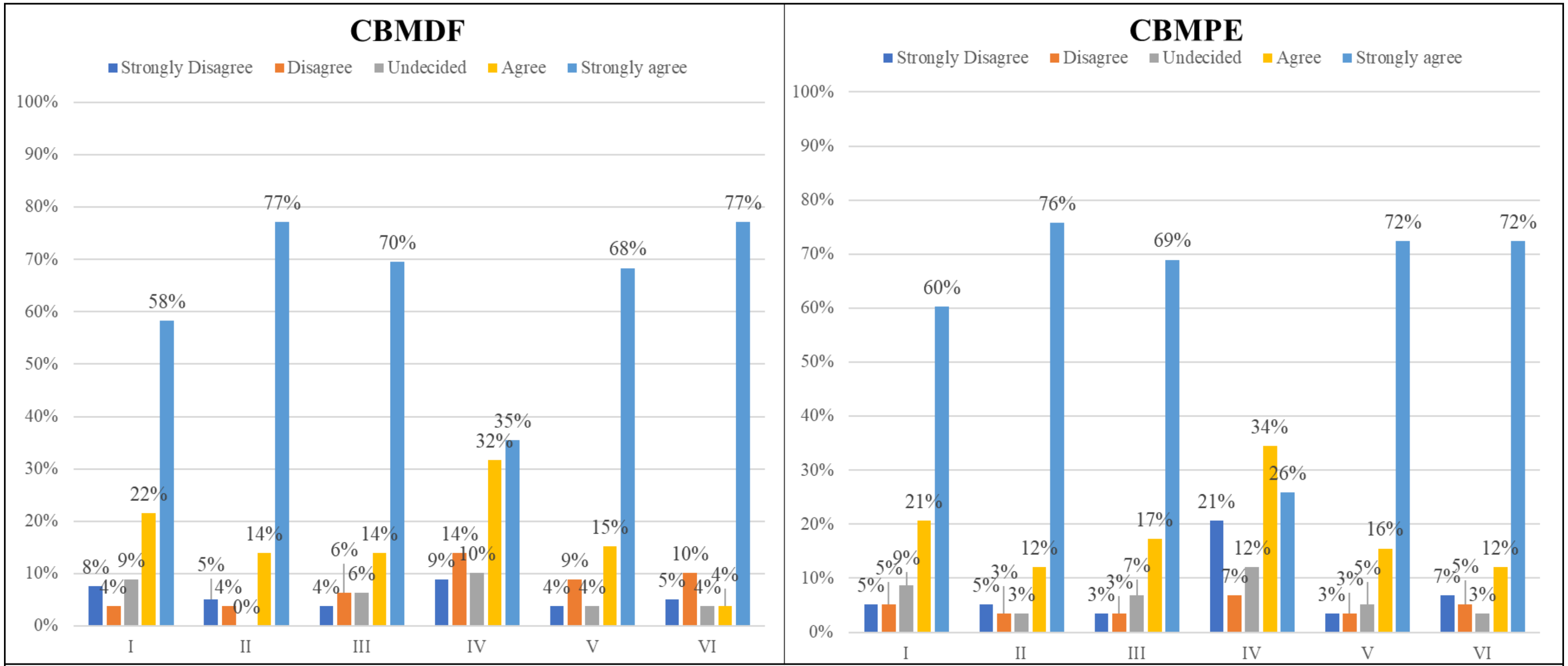


Graph 17. Provision of mechanisms/guidelines by the group to reduce the risk of cancer of research participants.



Graph 18. Provision of mechanisms/guidelines by the State to reduce the risk of cancer of research participants.

In the last part of the form, a Likert scale was used to evaluate the level of agreement with some statements related to cancer prevention. The answers were summarized in Graph 19.



I: I am concerned about the risk of developing cancer due to my profession.
II: The correct use of PPE can reduce cancer risk.
III: Keep my PPE clean and stored in a separate place can reduce cancer risk.
IV: Wash the suit every time after a fire can decrease its durability.
V: Keep my PPE clean decreases the chances of contaminating co-workers.
VI: Wash the suit at home, along with other clothes, can contaminate my family or people that live with me

Graph 19. Perception of research participants regarding developing cancer.

In the first item, most of respondents agrees (about 80% of both groups) said they are concerned about developing cancer due to the carrier. However, there is about 10% that disagrees which can indicate firefighters who did not have access to information that confirms the problem of cancer development in firefighters. Also, it suggests the need of health awareness and promotion campaigns.

Concerning the relation between PPE correct use and cancer risk decrease, the majority strongly agrees (~77%) with the assertive and it is important because leads to a lower exposure to PAHs and VOCs during fire fights.

The third assertive is directed to the PPE storage place. About 70% strongly agrees that a specific place to PPE storing contributes to reduce cancer risk. Nonetheless, as evaluated in this study, only 49-63% has a specific locker inside the fire department to PPE storage. These facts show that even though firefighters understand the need of a specific locker to PPE, some firefighters do not have structure and personal lockers directed to PPE storage inside fire departments. Therefore, despite a good level of awareness, apparently, there is a lack of structure that allows the implementation of precepts that can reduce the risk of developing cancer.

The following item deals with the problem of turnout fibers degradation caused by recurring washes. For CBMDF, this item had the higher percentage of disagreement. 9% strongly disagrees and 14% disagrees that laundering can reduce the suit durability. For CBMPE, this value raised up to a 21% strongly disagrees and 7% disagrees. It reinforces the need campaigns and trainings, also the need of more equipment.

The fifth assertive highlights the possibility of contamination through co-worker’s contaminated PPE. Therefore, it is stimulated the argument that keeping the PPE clean contributes not only with the firefighter’s health, but also with his/her co-worker’s health. Most people (71% CBMDF and 77% CBMPE) strongly agrees with it.

Finally, the sixth item is related to the PPE cleaning place. It is remarkable that the great majority (72% CBMDF and 77% CBMPE) strongly agrees that cleaning the suits at home can cause harm. On the other hand, this research reveals that 52-74% clean their PPE at home. Consequently, these data (added to third item) suggest that firefighters have a good awareness level related to good habits, but there is some difficulty to put these habits in practice, probably because of the lack of structure inside fire departments.

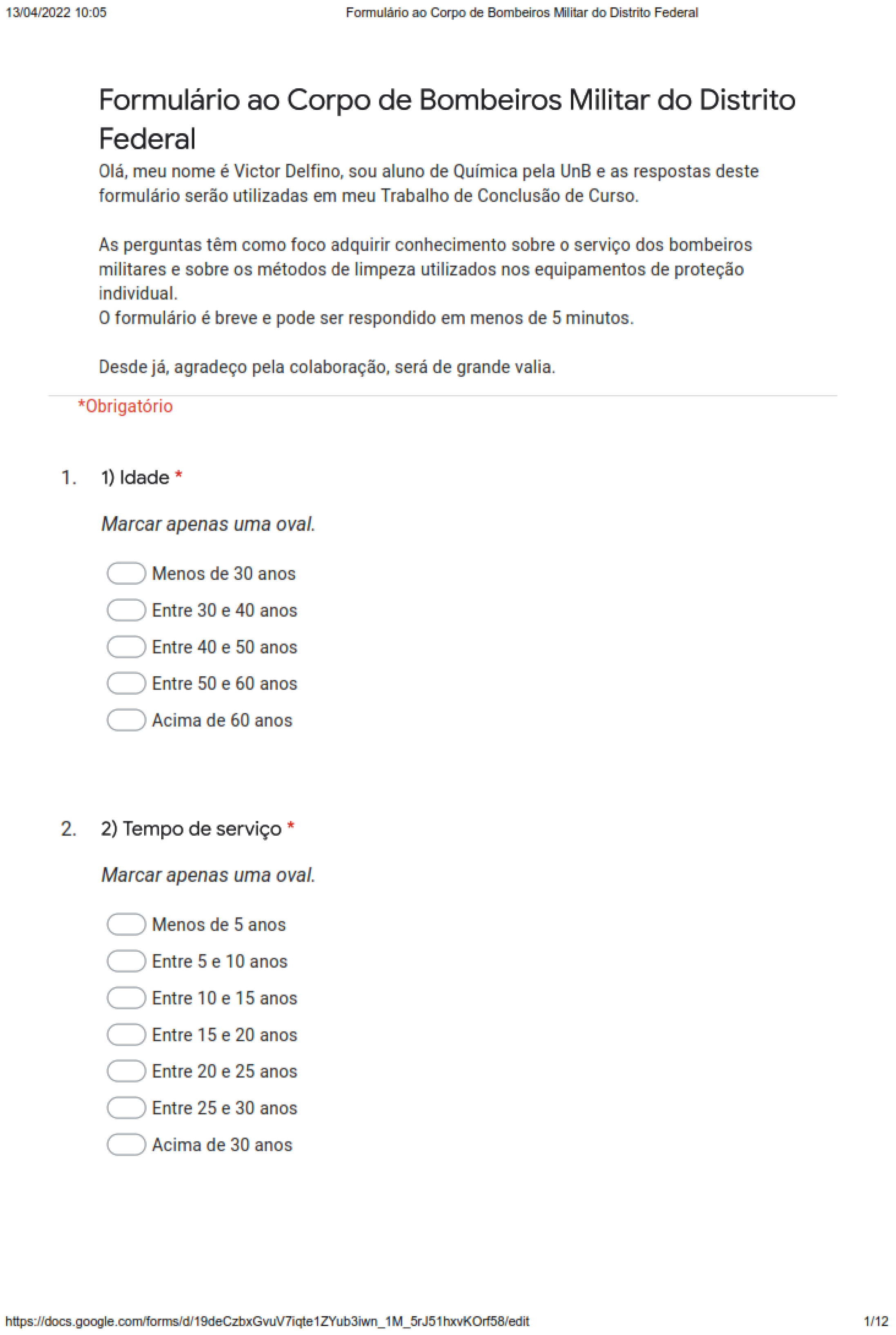
5. Conclusion and Perspectives

This study aimed to shed light on some Brazilians’ firefighters’ awareness about the increased risk of cancer development and on their practices regarding the cleaning and storage of their firefighting clothing. Conclusively, it is remarkable that contaminated PPE is one of the sources of exposure to carcinogens. Therefore, firefighter attitudes and behaviors toward post-fire decontamination processes can decrease their risk of developing cancer.

We observed awareness on the part of the firefighters who participated in the survey, related to the risk of developing cancer. They were aware that some practices such as the correct care of PPE and its frequent cleaning could reduce this risk. Even so, the survey indicated difficulty in adopting correct practices especially due to lack of training, information, and infrastructure. An incompatibility with the work routine was also a problem, especially when most of firefighters had only one suit. Despite awareness, and very probably due to lack of facilities, the firefighters' suits were stored in inappropriate places and cleaned infrequently. Also, a lack of information, training, and guidance inside fire departments to reduce cancer risk was pointed out by participants, suggesting that there is still a long way to go in the sense of promoting the occupational health of firefighters in Brazil.

6. Appendix

6.1. Google Forms platform form to the *Corpo de Bombeiros Militar do Distrito Federal.*



13/04/2022 10:05 Formulário ao Corpo de Bombeiros Militar do Distrito Federal

Formulário ao Corpo de Bombeiros Militar do Distrito Federal

Olá, meu nome é Victor Delfino, sou aluno de Química pela UnB e as respostas deste formulário serão utilizadas em meu Trabalho de Conclusão de Curso.

As perguntas têm como foco adquirir conhecimento sobre o serviço dos bombeiros militares e sobre os métodos de limpeza utilizados nos equipamentos de proteção individual.
O formulário é breve e pode ser respondido em menos de 5 minutos.

Desde já, agradeço pela colaboração, será de grande valia.

*Obrigatório

1. 1) Idade *

Marcar apenas uma oval.

○ Menos de 30 anos
○ Entre 30 e 40 anos
○ Entre 40 e 50 anos
○ Entre 50 e 60 anos
○ Acima de 60 anos

2. 2) Tempo de serviço *

Marcar apenas uma oval.

○ Menos de 5 anos
○ Entre 5 e 10 anos
○ Entre 10 e 15 anos
○ Entre 15 e 20 anos
○ Entre 20 e 25 anos
○ Entre 25 e 30 anos
○ Acima de 30 anos

https://docs.google.com/forms/d/19deCzbxGvuV7iqte1ZYub3iwn_1M_5rJ51hxvKOrf58/edit 1/12

13/04/2022 10:05 Formulário ao Corpo de Bombeiros Militar do Distrito Federal

3. 3) A qual Grupamento de Bombeiro Militar pertence *

Marque todas que se aplicam.

- ☐ 1º Brasília
- ☐ 2º Taguatinga
- ☐ 3 º SIA
- ☐ 4º Asa Norte
- ☐ 5º Aeroporto
- ☐ 6º Núcleo Bandeirante
- ☐ 7º Brazlândia
- ☐ 8º Ceilândia
- ☐ 9º Planaltina
- ☐ 10º Paranoá
- ☐ 11º Lago Sul
- ☐ 12º Samambaia
- ☐ 13º Guará 1
- ☐ 14º Cruzeiro
- ☐ 15º Asa Sul
- ☐ 16º Gama
- ☐ 17º São Sebastião
- ☐ 18º Santa Maria
- ☐ 19º Candangolândia
- ☐ 20º Recanto das Emas
- ☐ 21º Riacho Fundo
- ☐ 22º Sobradinho
- ☐ 23º Riacho Fundo II
- ☐ 24º Arniqueiras
- ☐ 25º Águas Claras
- ☐ 26º Br 070
- ☐ 27º Gama Oeste
- ☐ 28º Gama Sul
- ☐ 29º Grande Colorado
- ☐ 30º Guará II
- ☐ 31º Incra VIII
- ☐ 32º Itapuã
- ☐ 33º Jardim Botânico
- ☐ 34º Lago Norte
- ☐ 35º Park Way
- ☐ 36º Recanto das Emas Centro
- ☐ 37º Samambaia Centro
- ☐ 38º Santa Maria Sul

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☐ 39º SAAN
☐ 40º Estrutural
☐ 41º St. de Indústrias de Ceilândia
☐ 42º Setor P Sul
☐ 43º SRTS
☐ 44º Sobradinho II
☐ 45º Octogonal/Sudoeste
☐ 46º Taguatinga Sul
☐ 47º Taguatinga Norte
☐ 48º Vale do Amanhecer
☐ 49º Varjão
☐ 50º Vicente Pires
☐ GPCIU
☐ GPRAM
Outro: ☐ ______________________________

4. 4) Graduação *

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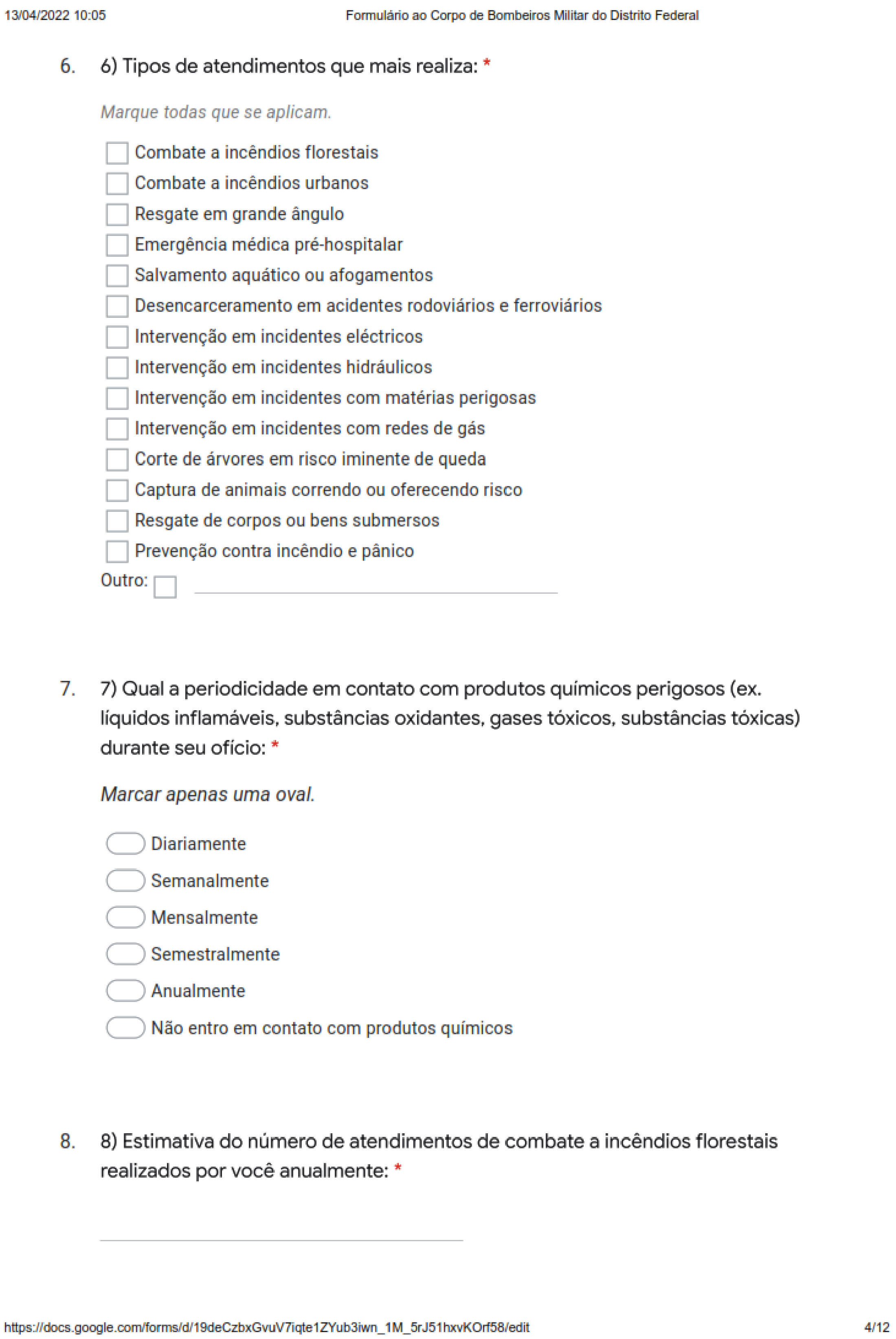
5. 5) Função

____



6. 6) Tipos de atendimentos que mais realiza: *

Marque todas que se aplicam.

☐ Combate a incêndios florestais
☐ Combate a incêndios urbanos
☐ Resgate em grande ângulo
☐ Emergência médica pré-hospitalar
☐ Salvamento aquático ou afogamentos
☐ Desencarceramento em acidentes rodoviários e ferroviários
☐ Intervenção em incidentes eléctricos
☐ Intervenção em incidentes hidráulicos
☐ Intervenção em incidentes com matérias perigosas
☐ Intervenção em incidentes com redes de gás
☐ Corte de árvores em risco iminente de queda
☐ Captura de animais correndo ou oferecendo risco
☐ Resgate de corpos ou bens submersos
☐ Prevenção contra incêndio e pânico
Outro: ☐ ____________________

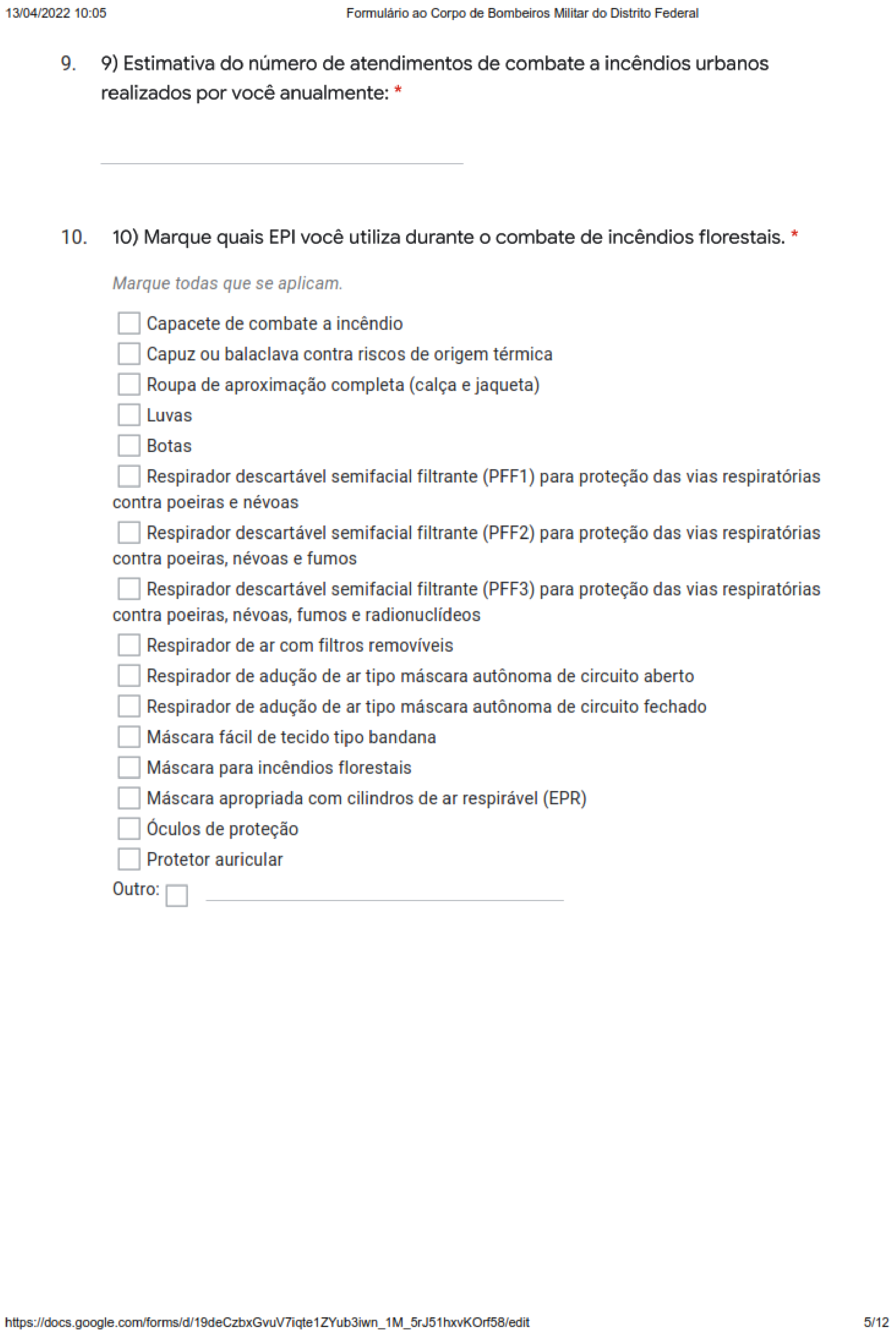
7. 7) Qual a periodicidade em contato com produtos químicos perigosos (ex. líquidos inflamáveis, substâncias oxidantes, gases tóxicos, substâncias tóxicas) durante seu ofício: *

Marcar apenas uma oval.

○ Diariamente
○ Semanalmente
○ Mensalmente
○ Semestralmente
○ Anualmente
○ Não entro em contato com produtos químicos

8. 8) Estimativa do número de atendimentos de combate a incêndios florestais realizados por você anualmente: *

____



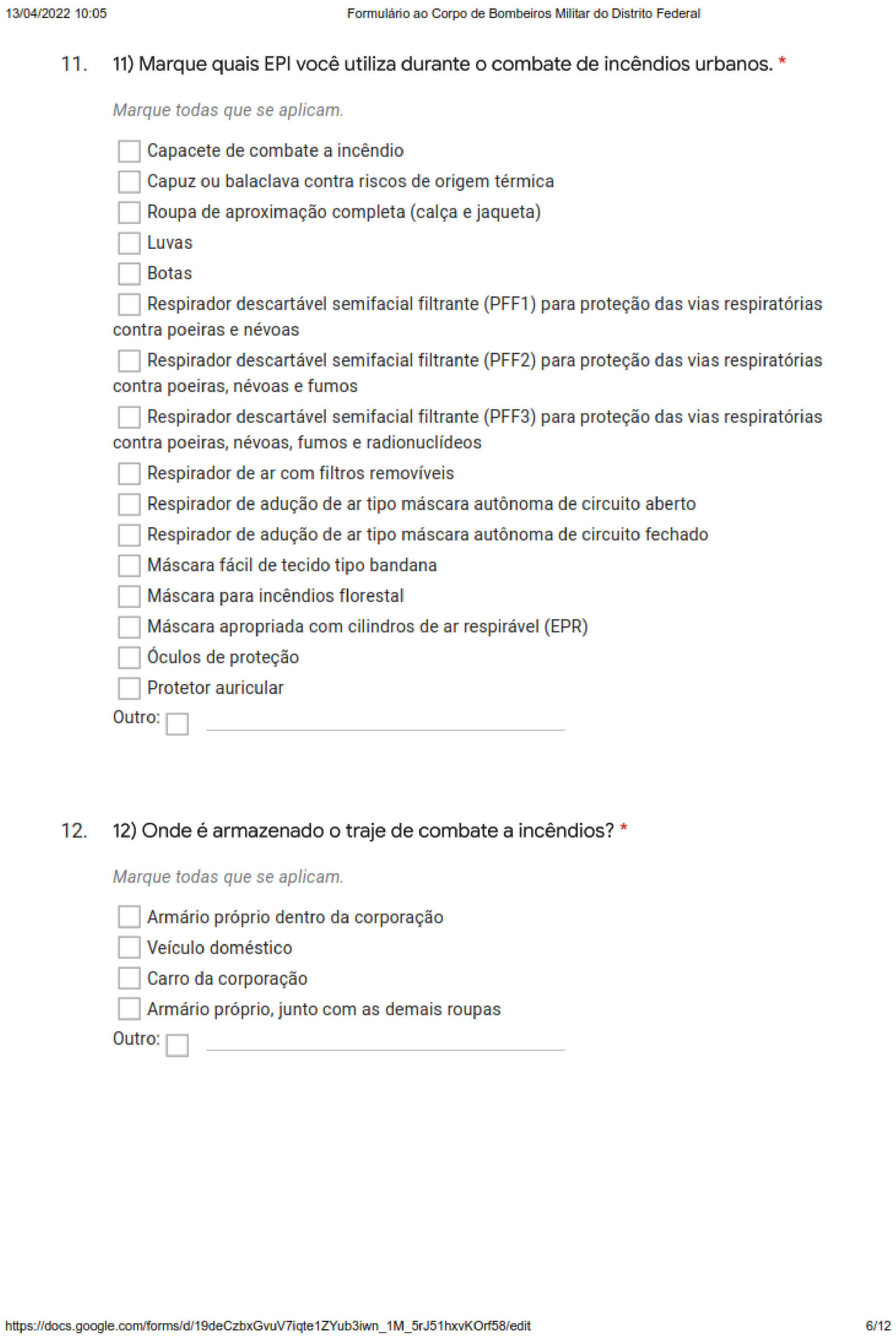
9. 9) Estimativa do número de atendimentos de combate a incêndios urbanos realizados por você anualmente: *

____

10. 10) Marque quais EPI você utiliza durante o combate de incêndios florestais. *

Marque todas que se aplicam.

☐ Capacete de combate a incêndio
☐ Capuz ou balaclava contra riscos de origem térmica
☐ Roupa de aproximação completa (calça e jaqueta)
☐ Luvas
☐ Botas
☐ Respirador descartável semifacial filtrante (PFF1) para proteção das vias respiratórias contra poeiras e névoas
☐ Respirador descartável semifacial filtrante (PFF2) para proteção das vias respiratórias contra poeiras, névoas e fumos
☐ Respirador descartável semifacial filtrante (PFF3) para proteção das vias respiratórias contra poeiras, névoas, fumos e radionuclídeos
☐ Respirador de ar com filtros removíveis
☐ Respirador de adução de ar tipo máscara autônoma de circuito aberto
☐ Respirador de adução de ar tipo máscara autônoma de circuito fechado
☐ Máscara fácil de tecido tipo bandana
☐ Máscara para incêndios florestais
☐ Máscara apropriada com cilindros de ar respirável (EPR)
☐ Óculos de proteção
☐ Protetor auricular
Outro: ☐ ________________________________



11. 11) Marque quais EPI você utiliza durante o combate de incêndios urbanos. *

Marque todas que se aplicam.

☐ Capacete de combate a incêndio
☐ Capuz ou balaclava contra riscos de origem térmica
☐ Roupa de aproximação completa (calça e jaqueta)
☐ Luvas
☐ Botas
☐ Respirador descartável semifacial filtrante (PFF1) para proteção das vias respiratórias contra poeiras e névoas
☐ Respirador descartável semifacial filtrante (PFF2) para proteção das vias respiratórias contra poeiras, névoas e fumos
☐ Respirador descartável semifacial filtrante (PFF3) para proteção das vias respiratórias contra poeiras, névoas, fumos e radionuclídeos
☐ Respirador de ar com filtros removíveis
☐ Respirador de adução de ar tipo máscara autônoma de circuito aberto
☐ Respirador de adução de ar tipo máscara autônoma de circuito fechado
☐ Máscara fácil de tecido tipo bandana
☐ Máscara para incêndios florestal
☐ Máscara apropriada com cilindros de ar respirável (EPR)
☐ Óculos de proteção
☐ Protetor auricular
Outro: ☐ ____________________

12. 12) Onde é armazenado o traje de combate a incêndios? *

Marque todas que se aplicam.

☐ Armário próprio dentro da corporação
☐ Veículo doméstico
☐ Carro da corporação
☐ Armário próprio, junto com as demais roupas
Outro: ☐ ____________________

13. 13) Em qual local é realizada a lavagem do seu traje de combate a incêndios? *

Marque todas que se aplicam.

- ☐ No quartel
- ☐ Em casa
- ☐ Em lavanderia comercial
- ☐ Em lavanderia especializada

Outro: ☐ ____________________

14. 14) Como é feita a lavagem do seu traje de combate a incêndios? *

Marque todas que se aplicam.

- ☐ Lenços umedecidos
- ☐ Somente com água pressurizada
- ☐ Somente com água corrente
- ☐ Água e sabão
- ☐ Extratores específicos
- ☐ Separada das demais roupas
- ☐ Junto com as demais roupas

Outro: ☐ ____________________

15. 15) Como é feita a descontaminação dos equipamentos utilizados no combate a incêndios? Se possível, descreva o método: *

16. 16) Você faz algum tipo de higienização após o combate de um incêndio? Se sim, como? *

Marque todas que se aplicam.

☐ Toma banho
☐ Limpeza com lenços umedecidos do corpo
☐ Limpeza do traje de combate com lenços umedecidos
☐ Lavagem do traje de combate
☐ Não realiza nenhum tipo de higienização
Outro: ☐ ____________________

17. 17) Quantos trajes de combate a incêndio possui? *

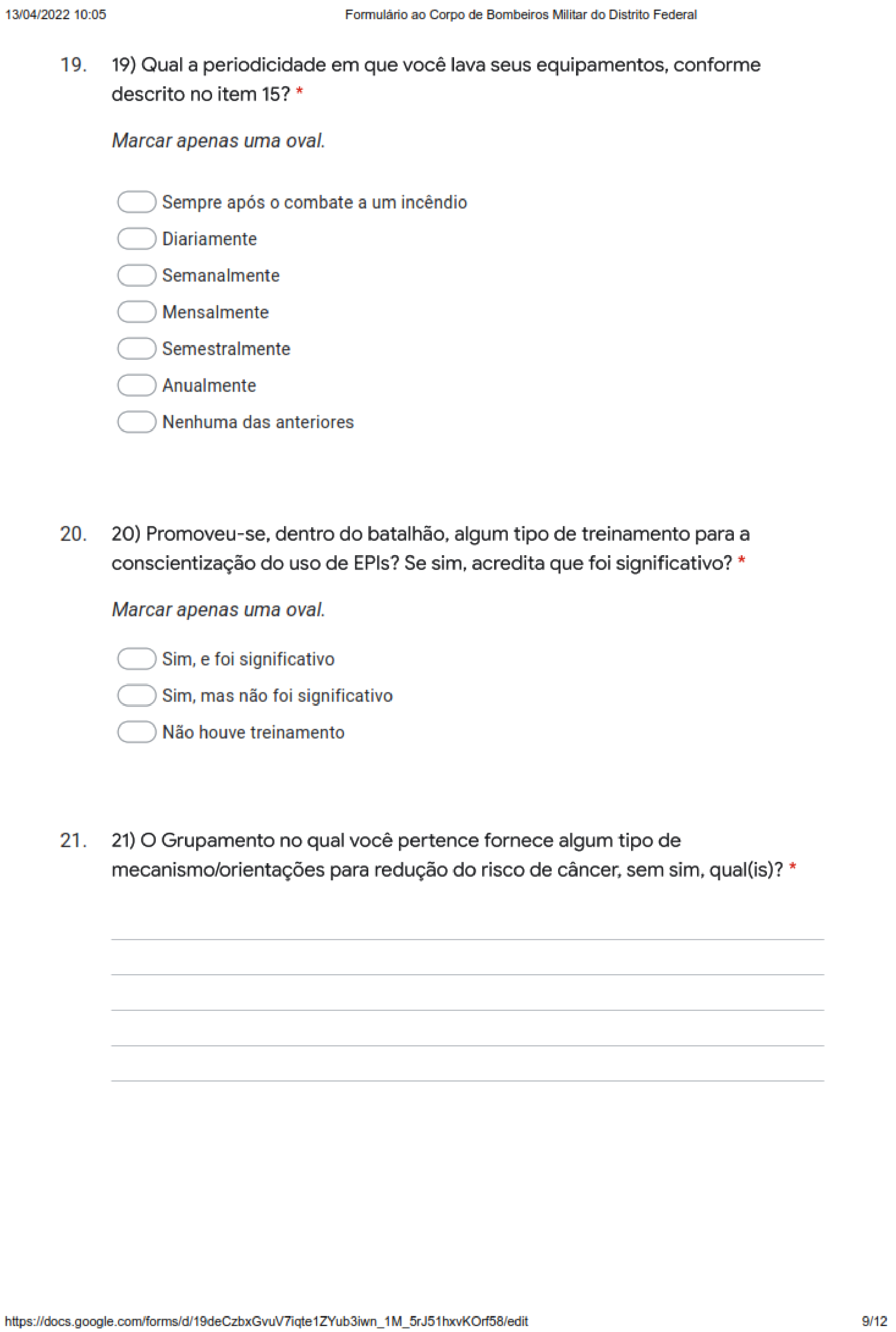
Marcar apenas uma oval.

○ Zero
○ 1
○ 2
○ 3
○ 4 ou mais trajes

18. 18) Qual a periodicidade em que você lava o seu traje de combate a incêndios, conforme descrito no item 14? *

Marcar apenas uma oval.

○ Sempre após o combate a um incêndio
○ Diariamente
○ Semanalmente
○ Mensalmente
○ Semestralmente
○ Anualmente
○ Nenhuma das anteriores



19. 19) Qual a periodicidade em que você lava seus equipamentos, conforme descrito no item 15? *

Marcar apenas uma oval.

○ Sempre após o combate a um incêndio
○ Diariamente
○ Semanalmente
○ Mensalmente
○ Semestralmente
○ Anualmente
○ Nenhuma das anteriores

20. 20) Promoveu-se, dentro do batalhão, algum tipo de treinamento para a conscientização do uso de EPIs? Se sim, acredita que foi significativo? *

Marcar apenas uma oval.

○ Sim, e foi significativo
○ Sim, mas não foi significativo
○ Não houve treinamento

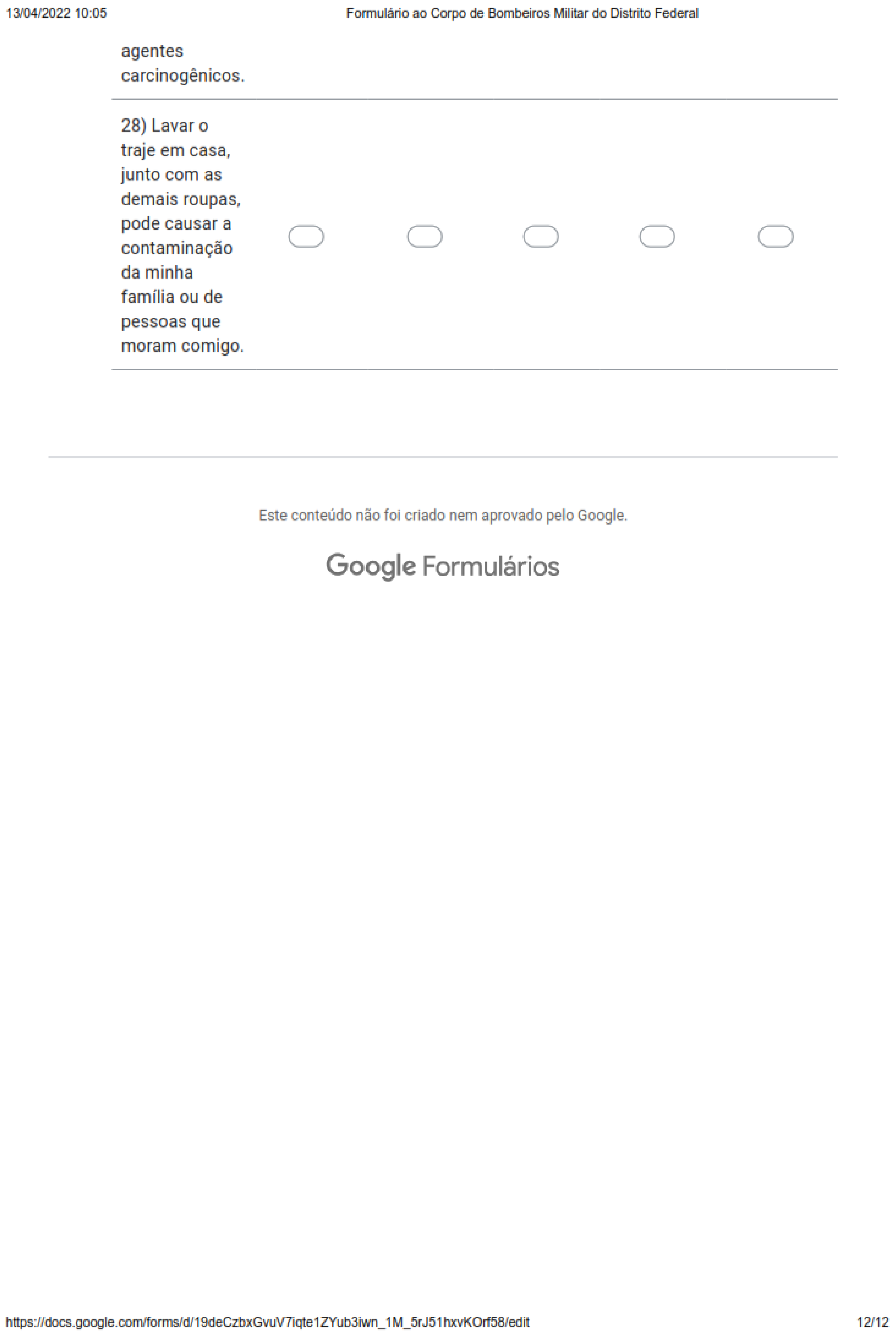
21. 21) O Grupamento no qual você pertence fornece algum tipo de mecanismo/orientações para redução do risco de câncer, sem sim, qual(is)? *

22. 22) O Estado fornece mecanismo/orientações para redução do risco de câncer, se sim, qual(is)? *

23. *

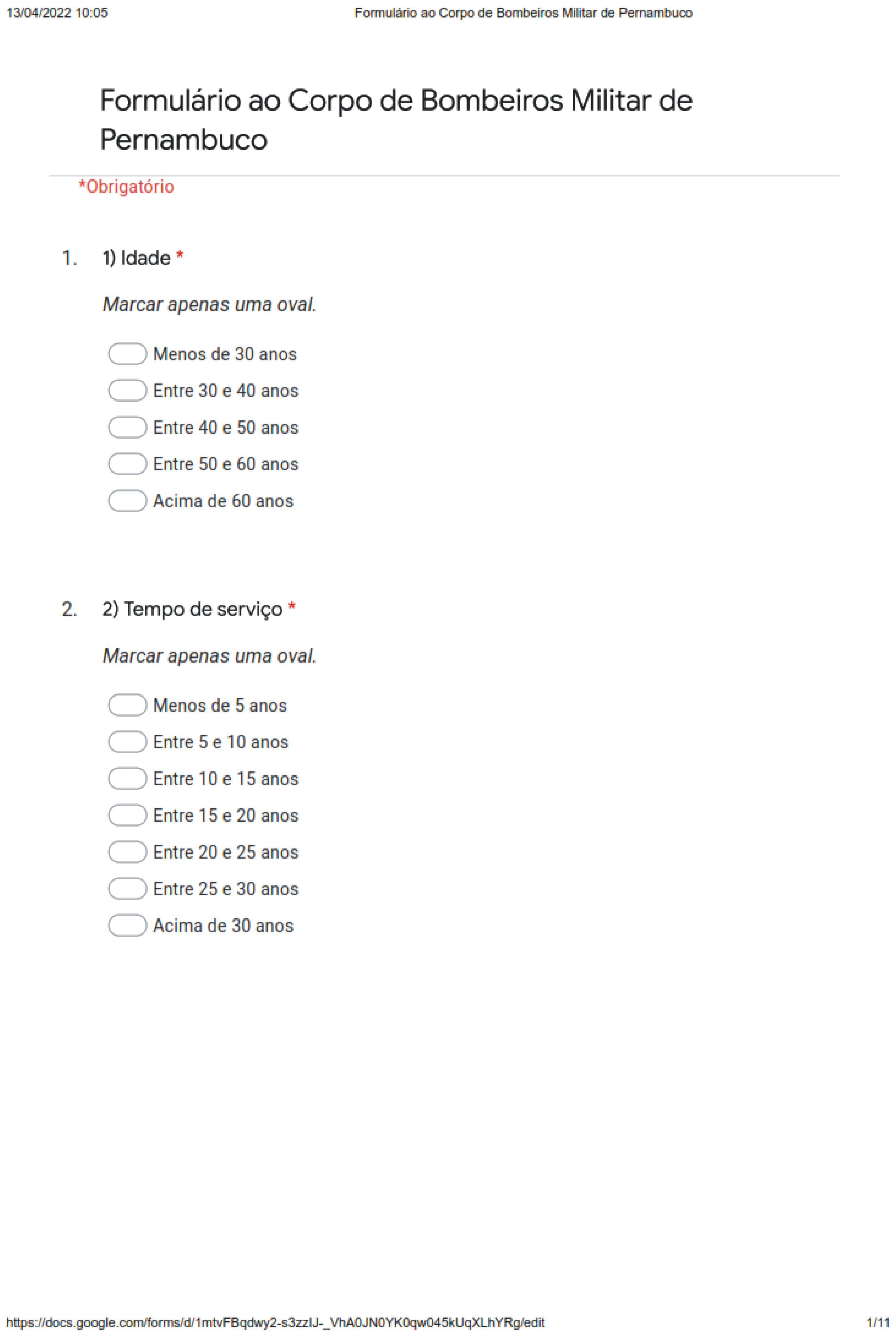
Marcar apenas uma oval por linha.

	Discordo Totalmente	Discordo Parcialmente	Indiferente	Concordo Parcialmente	Concordo Totalmente
23) Estou preocupado(a) com o risco de desenvolver câncer devido à minha profissão.	○	○	○	○	○
24) O uso de EPI correto pode reduzir o risco de desenvolver câncer.	○	○	○	○	○
25) Manter meus EPIs higienizados e armazenados em um local separado pode reduzir o risco de desenvolver câncer.	○	○	○	○	○
26) Realizar a lavagem dos trajes após todos os combates a incêndios pode diminuir a durabilidade destes.	○	○	○	○	○
27) Manter meu(s) traje(s) de combate a incêndios higienizados diminui as chances de contaminação de colegas de trabalho por	○	○	○	○	○



agentes carcinogênicos.					
28) Lavar o traje em casa, junto com as demais roupas, pode causar a contaminação da minha família ou de pessoas que moram comigo.	○	○	○	○	○

6.2. Google Forms platform form to the *Corpo de Bombeiros Militar do Pernambuco*.



13/04/2022 10:05 Formulário ao Corpo de Bombeiros Militar de Pernambuco

Formulário ao Corpo de Bombeiros Militar de Pernambuco

*Obrigatório

1. 1) Idade *

Marcar apenas uma oval.

○ Menos de 30 anos
○ Entre 30 e 40 anos
○ Entre 40 e 50 anos
○ Entre 50 e 60 anos
○ Acima de 60 anos

2. 2) Tempo de serviço *

Marcar apenas uma oval.

○ Menos de 5 anos
○ Entre 5 e 10 anos
○ Entre 10 e 15 anos
○ Entre 15 e 20 anos
○ Entre 20 e 25 anos
○ Entre 25 e 30 anos
○ Acima de 30 anos

https://docs.google.com/forms/d/1mtvFBqdwy2-s3zzlJ-_VhA0JN0YK0qw045kUqXLhYRg/edit 1/11

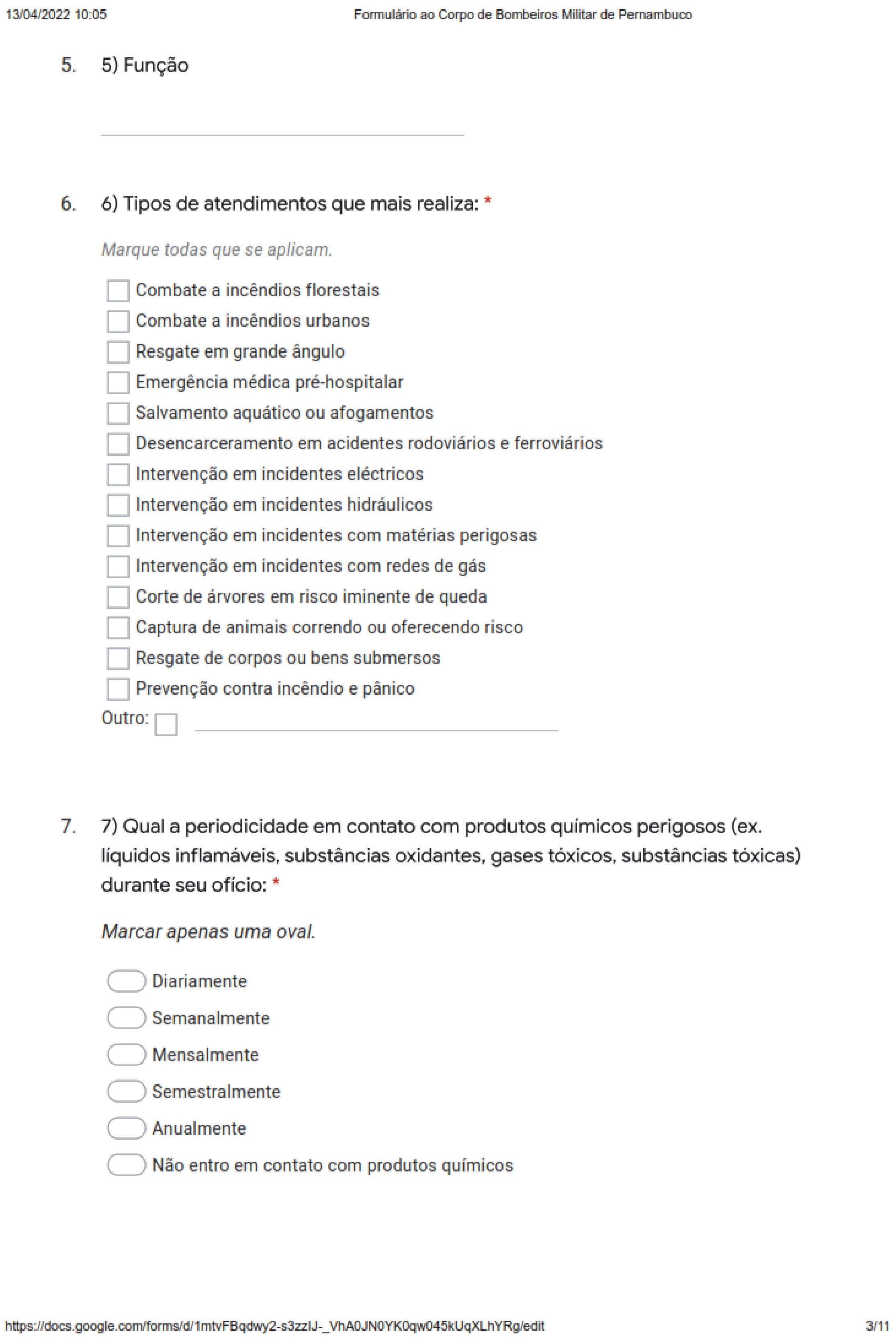
3. 3) A qual Quartel de Bombeiro Militar pertence *

Marque todas que se aplicam.

☐ QUARTEL DO COMANDO GERAL
☐ CENTRO DE ASSISTÊNCIA SOCIAL
☐ DIRETORIA INTEGRADA METROPOLITANA
☐ DIRETORIA INTEGRADA DO INTERIOR
☐ CAMPUS DE ENSINO METROPOLITANO II
☐ CENTRO DE MANUTENÇÃO
☐ GRUPAMENTO DE BOMBEIROS DE SALVAMENTO
☐ SEÇÃO DE BOMBEIROS DE FERNANDO DE NORONHA
☐ GRUPAMENTO DE BOMBEIROS DE ATENDIMENTO PRÉ-HOSPITALAR
☐ SEÇÃO DE BOMBEIROS DE IGARASSU
☐ SEÇÃO DE BOMBEIROS DE SÃO LOURENÇO DA MATA
☐ GRUPAMENTO DE BOMBEIROS DE INCÊNDIO
☐ 2ª SEÇÃO DE BOMBEIROS DE INCÊNDIO
☐ SEÇÃO DE BOMBEIROS DE SUAPE
☐ SEÇÃO DE BOMBEIROS DA INFRAERO
☐ GRUPAMENTO DE BOMBEIROS MARÍTMO
☐ SEÇÃO DE BOMBEIROS DE JARDIM ATLÂNTICO
☐ 1º GRUPAMENTO DE BOMBEIROS
☐ SEÇÃO DE BOMBEIROS DE PALMARES
☐ SEÇÃO DE BOMBEIROS DE GOIANA
☐ 2º GRUPAMENTO DE BOMBEIROS
☐ SEÇÃO DE BOMBEIROS DE GRAVATÁ
☐ SEÇÃO DE BOMBEIROS DE BEZERROS
☐ SEÇÃO DE BOMBEIROS DE SANTA CRUZ DO CAPIBARIBE
☐ 3º GRUPAMENTO DE BOMBEIROS
☐ SEÇÃO DE BOMBEIROS DE PETROLÂNDIA
☐ 4º GRUPAMENTO DE BOMBEIROS
☐ 5º GRUPAMENTO DE BOMBEIROS
☐ SEÇÃO DE BOMBEIROS DE OURICURI
☐ 6º GRUPAMENTO DE BOMBEIROS
☐ SEÇÃO DE BOMBEIROS DE BELO JARDIM
Outro: ☐ ____________________

4. 4) Graduação *

____



5. 5) Função

6. 6) Tipos de atendimentos que mais realiza: *

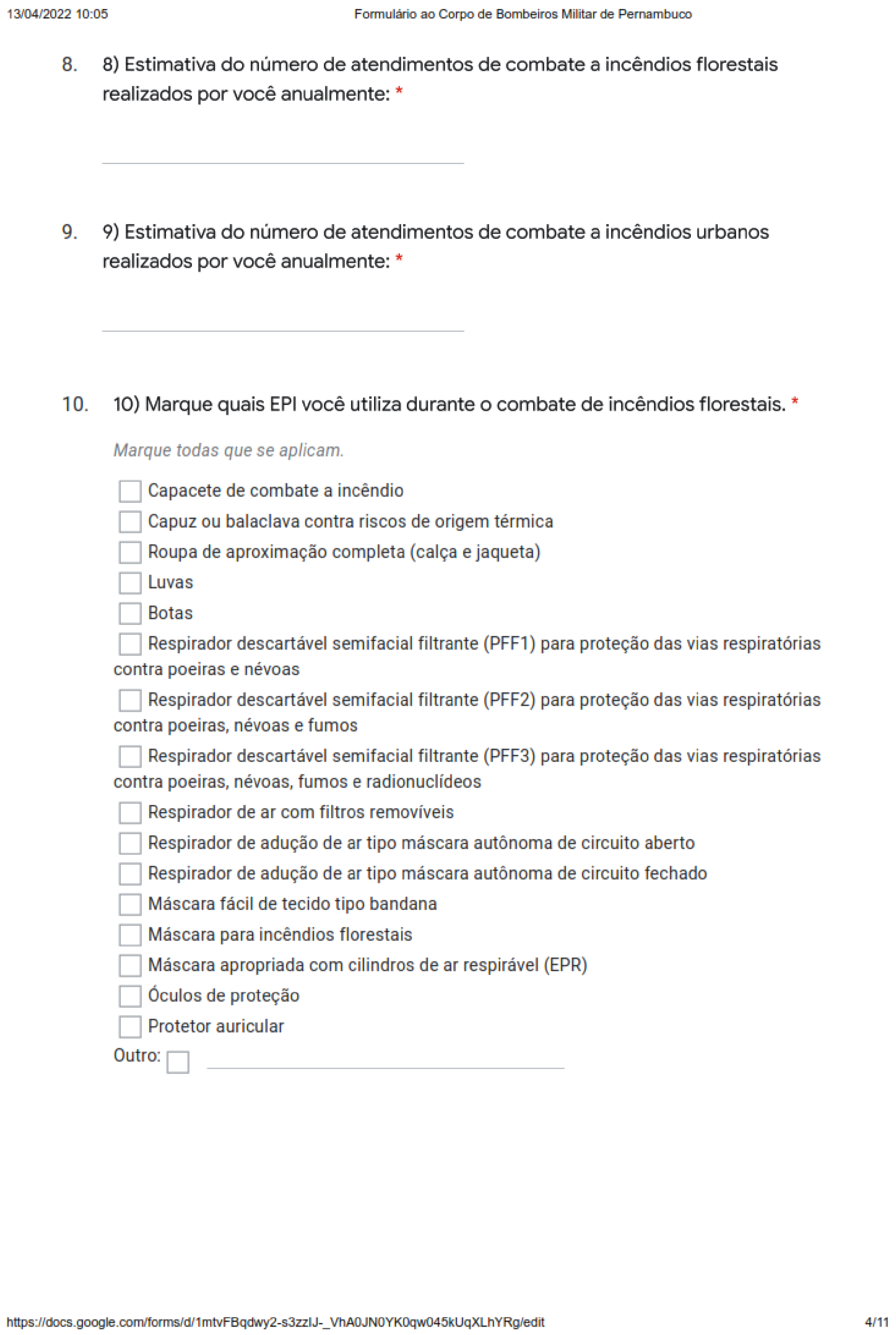
Marque todas que se aplicam.

☐ Combate a incêndios florestais
☐ Combate a incêndios urbanos
☐ Resgate em grande ângulo
☐ Emergência médica pré-hospitalar
☐ Salvamento aquático ou afogamentos
☐ Desencarceramento em acidentes rodoviários e ferroviários
☐ Intervenção em incidentes eléctricos
☐ Intervenção em incidentes hidráulicos
☐ Intervenção em incidentes com matérias perigosas
☐ Intervenção em incidentes com redes de gás
☐ Corte de árvores em risco iminente de queda
☐ Captura de animais correndo ou oferecendo risco
☐ Resgate de corpos ou bens submersos
☐ Prevenção contra incêndio e pânico
Outro: ☐

7. 7) Qual a periodicidade em contato com produtos químicos perigosos (ex. líquidos inflamáveis, substâncias oxidantes, gases tóxicos, substâncias tóxicas) durante seu ofício: *

Marcar apenas uma oval.

○ Diariamente
○ Semanalmente
○ Mensalmente
○ Semestralmente
○ Anualmente
○ Não entro em contato com produtos químicos



8. 8) Estimativa do número de atendimentos de combate a incêndios florestais realizados por você anualmente: *

9. 9) Estimativa do número de atendimentos de combate a incêndios urbanos realizados por você anualmente: *

10. 10) Marque quais EPI você utiliza durante o combate de incêndios florestais. *

Marque todas que se aplicam.

☐ Capacete de combate a incêndio
☐ Capuz ou balaclava contra riscos de origem térmica
☐ Roupa de aproximação completa (calça e jaqueta)
☐ Luvas
☐ Botas
☐ Respirador descartável semifacial filtrante (PFF1) para proteção das vias respiratórias contra poeiras e névoas
☐ Respirador descartável semifacial filtrante (PFF2) para proteção das vias respiratórias contra poeiras, névoas e fumos
☐ Respirador descartável semifacial filtrante (PFF3) para proteção das vias respiratórias contra poeiras, névoas, fumos e radionuclídeos
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☐ Respirador de adução de ar tipo máscara autônoma de circuito fechado
☐ Máscara fácil de tecido tipo bandana
☐ Máscara para incêndios florestais
☐ Máscara apropriada com cilindros de ar respirável (EPR)
☐ Óculos de proteção
☐ Protetor auricular
Outro: ☐

11. 11) Marque quais EPI você utiliza durante o combate de incêndios urbanos. *

Marque todas que se aplicam.

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☐ Capuz ou balaclava contra riscos de origem térmica
☐ Roupa de aproximação completa (calça e jaqueta)
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☐ Botas
☐ Respirador descartável semifacial filtrante (PFF1) para proteção das vias respiratórias contra poeiras e névoas
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☐ Respirador descartável semifacial filtrante (PFF3) para proteção das vias respiratórias contra poeiras, névoas, fumos e radionuclídeos
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☐ Respirador de adução de ar tipo máscara autônoma de circuito fechado
☐ Máscara fácil de tecido tipo bandana
☐ Máscara para incêndios florestal
☐ Máscara apropriada com cilindros de ar respirável (EPR)
☐ Óculos de proteção
☐ Protetor auricular
Outro: ☐ ____________________

12. 12) Onde é armazenado o traje de combate a incêndios? *

Marque todas que se aplicam.

☐ Armário próprio dentro da corporação
☐ Veículo doméstico
☐ Carro da corporação
☐ Armário próprio, junto com as demais roupas
Outro: ☐ ____________________

13. 13) Em qual local é realizada a lavagem do seu traje de combate a incêndios? *

Marque todas que se aplicam.

☐ No quartel
☐ Em casa
☐ Em lavanderia comercial
☐ Em lavanderia especializada
Outro: ☐ ____________________

14. 14) Como é feita a lavagem do seu traje de combate a incêndios? *

Marque todas que se aplicam.

☐ Lenços umedecidos
☐ Somente com água pressurizada
☐ Somente com água corrente
☐ Água e sabão
☐ Extratores específicos
☐ Separada das demais roupas
☐ Junto com as demais roupas
Outro: ☐ ____________________

15. 15) Como é feita a descontaminação dos equipamentos utilizados no combate a incêndios? Se possível, descreva o método: *

16. 16) Você faz algum tipo de higienização após o combate de um incêndio? Se sim, como? *

Marque todas que se aplicam.

- ☐ Toma banho
- ☐ Limpeza com lenços umedecidos do corpo
- ☐ Limpeza do traje de combate com lenços umedecidos
- ☐ Lavagem do traje de combate
- ☐ Não realiza nenhum tipo de higienização

Outro: ☐ ______________________

17. 17) Quantos trajes de combate a incêndio possui? *

Marcar apenas uma oval.

- ○ Zero
- ○ 1
- ○ 2
- ○ 3
- ○ 4 ou mais trajes

18. 18) Qual a periodicidade em que você lava o seu traje de combate a incêndios, conforme descrito no item 14? *

Marcar apenas uma oval.

- ○ Sempre após o combate a um incêndio
- ○ Diariamente
- ○ Semanalmente
- ○ Mensalmente
- ○ Semestralmente
- ○ Anualmente
- ○ Nenhuma das anteriores

19. 19) Qual a periodicidade em que você lava seus equipamentos, conforme descrito no item 15? *

Marcar apenas uma oval.

- ○ Sempre após o combate a um incêndio
- ○ Diariamente
- ○ Semanalmente
- ○ Mensalmente
- ○ Semestralmente
- ○ Anualmente
- ○ Nenhuma das anteriores

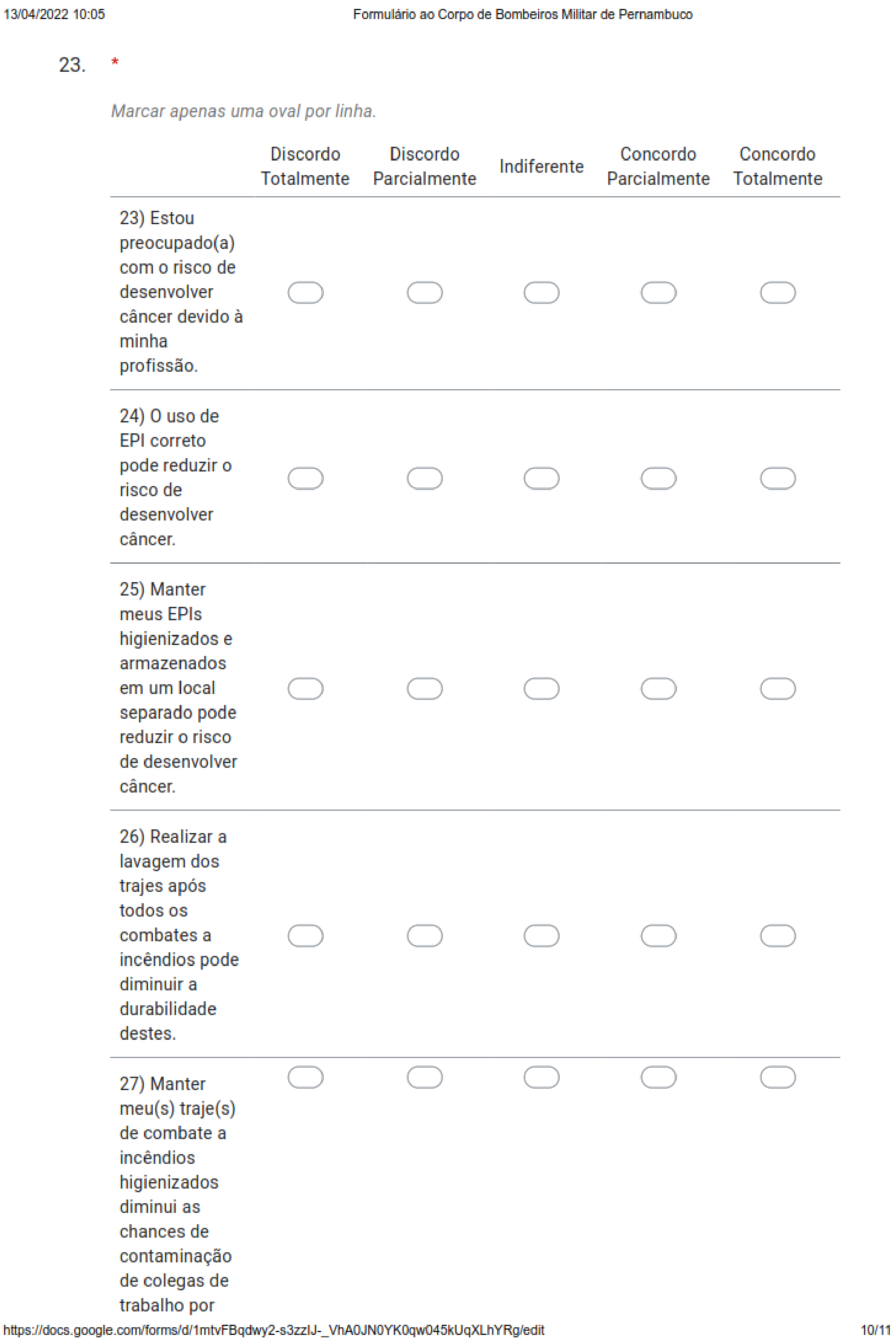
20. 20) Promoveu-se, dentro do batalhão, algum tipo de treinamento para a conscientização do uso de EPIs? Se sim, acredita que foi significativo? *

Marcar apenas uma oval.

- ○ Sim, e foi significativo
- ○ Sim, mas não foi significativo
- ○ Não houve treinamento

21. 21) O Grupamento no qual você pertence fornece algum tipo de mecanismo/orientações para redução do risco de câncer, sem sim, qual(is)? *

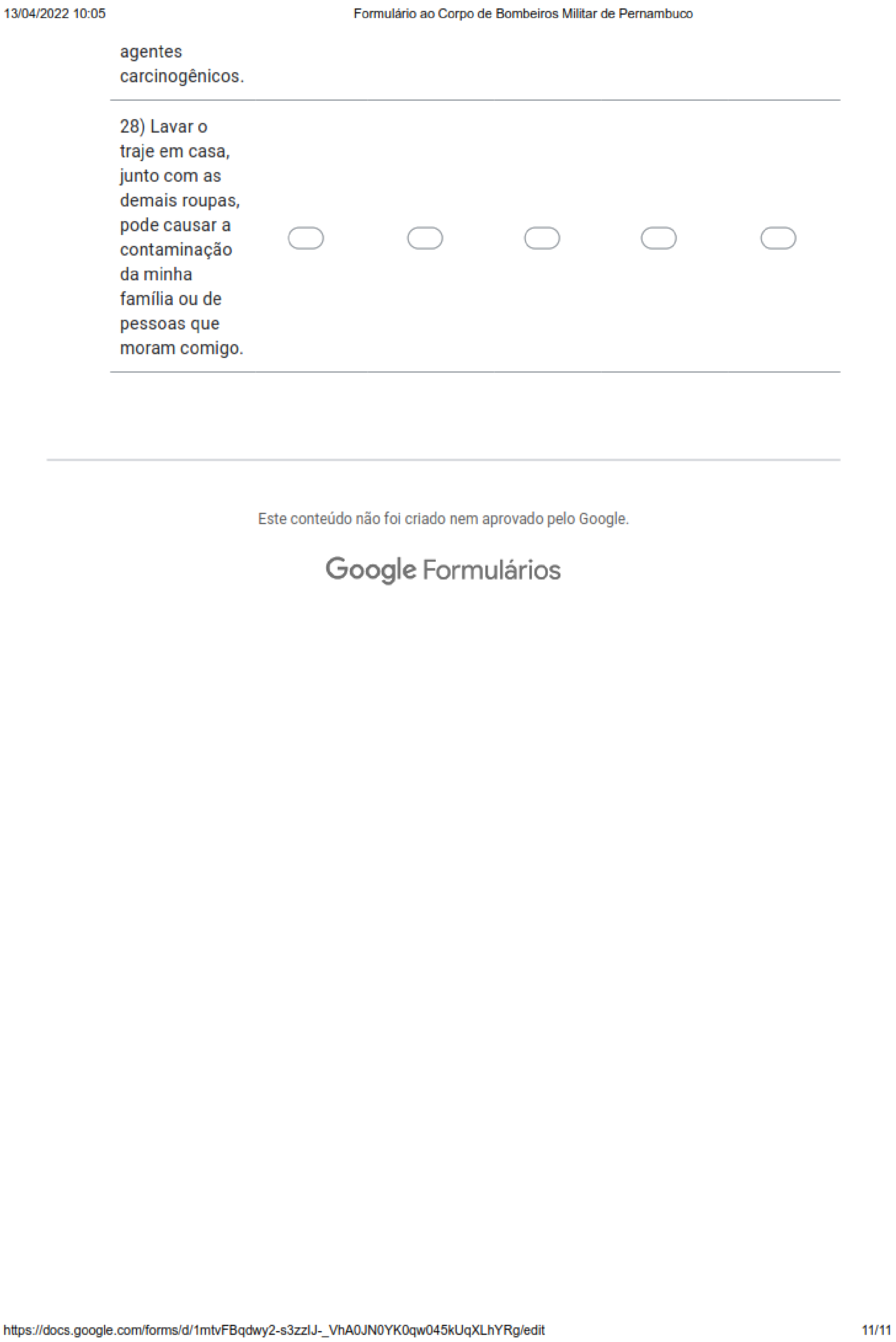
22. 22) O Estado fornece mecanismo/orientações para redução do risco de câncer, se sim, qual(is)? *



23. *

Marcar apenas uma oval por linha.

	Discordo Totalmente	Discordo Parcialmente	Indiferente	Concordo Parcialmente	Concordo Totalmente
23) Estou preocupado(a) com o risco de desenvolver câncer devido à minha profissão.	○	○	○	○	○
24) O uso de EPI correto pode reduzir o risco de desenvolver câncer.	○	○	○	○	○
25) Manter meus EPIs higienizados e armazenados em um local separado pode reduzir o risco de desenvolver câncer.	○	○	○	○	○
26) Realizar a lavagem dos trajes após todos os combates a incêndios pode diminuir a durabilidade destes.	○	○	○	○	○
27) Manter meu(s) traje(s) de combate a incêndios higienizados diminui as chances de contaminação de colegas de trabalho por	○	○	○	○	○



agentes carcinogênicos.					
28) Lavar o traje em casa, junto com as demais roupas, pode causar a contaminação da minha família ou de pessoas que moram comigo.	○	○	○	○	○

CHAPTER 2

POLYCYCLIC AROMATIC HYDROCARBON CONTAMINATION OF BRAZILIAN FIRFIGHTERS' PERSONAL PROTECTIVE EQUIPMENT DURING TRAINING EXERCISE

1. Theoretical reference

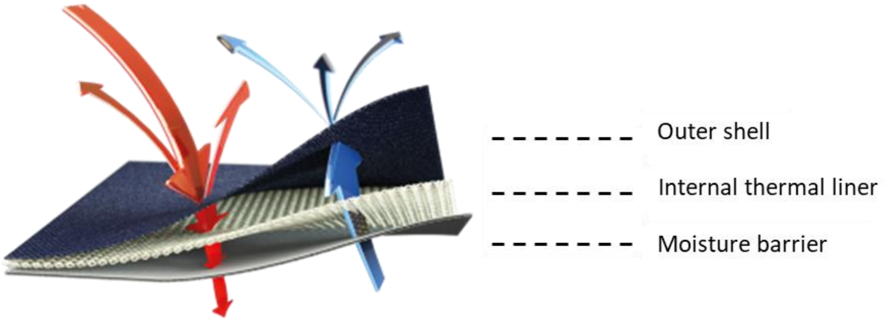
1.1. Proximity Firefighting Protective Clothing (PFPC)

Proximity Firefighting Protective Clothing (PFPC) is part of firefighters' PPE and allows thermal protection from the heat of the flames, as well as physical protection against sharp and pointed objects. The jacket and pants are part of the PFPC (Figure 7).

Source: www.texport.at/en/collections/fireware/

Figure 7. Proximity Firefighting Protective Clothing: pants and jacket[79].

PFPC are generally made in three layers: outer layer, middle layer and membrane, each with specific properties. The layers (Figure 8) are developed from fiber blends of aromatic polyamides. The first layer, called the outer shell, has the function of promoting thermal protection and physical protection. Therefore, it is usually composed of a mixture of Nomex®, Kevlar® and carbon. The middle layer (internal thermal liner) mainly promotes thermal protection, in addition to allowing the exchange of heat through perspiration. The last layer (moisture barrier) consists of an impermeable membrane, which blocks the entry of water and other toxic substances, having in its composition the Teflon® polymer (polytetrafluoroethylene). This configuration reduces heat and water penetration in the turnout gear (red arrows Figure 8) and allows the skin to breathe (blue arrows Figure 8)



Source: www.texport.at/en/collections/fireware/

Figure 8. PFPC shells[79].

Kevlar® is a lightweight, heat-resistant, synthetic para-aramid fiber that offers high tensile strength and thermal protection. In its molecular structure, Figure 9a, its interchain links are responsible for its high shear and puncture resistance. It was developed in 1965 by Stephanie Kwolek and is a registered trademark of DuPont [80].

Another compound that is a registered trademark of the chemical company DuPont is Nomex®. Meta-aramid fiber, Figure 9b, has high heat and flame resistance, does not melt, drip or burn. Given these characteristics, it is the main component of firefighter PPE[81].

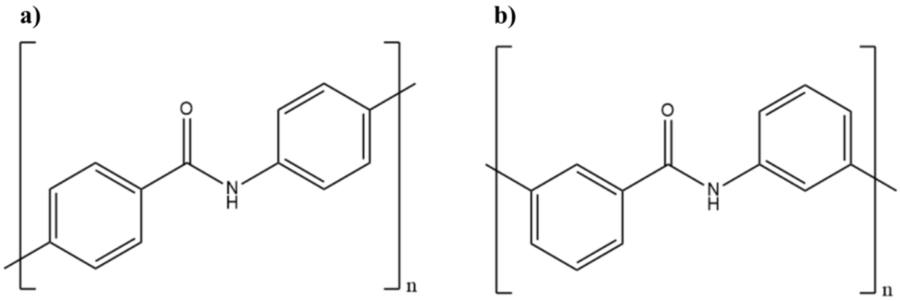


Figure 9. Structure of the polymers **(a)** para-aramid and **(b)** meta-aramid.

1.2.PAHs in firefighter PPE

The occupational exposure of firefighters to PAHs causes the various effects described previously and the presence of these compounds is described in the literature. Contamination of firefighters' PPE during firefighting was demonstrated in a study carried out by Fent *et al.*[64]. In this study, swabs were collected from PPE before and after fighting a simulated residential fire, and the concentration of pollutants increased after each response to a firefighting call. There was a higher deposition in firefighters who carried out the fire attack activity, when compared to those who carried out search and rescue activities.

Contamination of gloves and hoods was also assessed. The compounds benzo[a]anthracene and benzo[a]pyrene were found in firefighter equipment of the Chicago Fire Department[21]. In the study, contamination was evaluated for four months, and PPEs were randomly selected and analyzed to identify contaminants, both organic and inorganic. In another work, Stec *et al.*[82] evaluated the presence of the 19 PAHs deposited on the skin of firefighters (jaw, neck and hands), in PPE and in common areas of departments (offices, fire stations and engines). Carcinogenic PAHs were found in all tested areas.

In addition to PPE, the presence of PAH biomarkers were found in the urine of participants after firefighting training. Fent[83] determined that continuous exposure in training may increase the risk of developing cancer, especially in instructors, who have a greater exposure than firefighters on duty. In this perspective, the presence of these compounds in firefighters' PPE and in in common areas of fire departments is a concerning fact because it favors the cross-contamination, increasing the risk of developing diseases related to exposure to fire residues [83]

In Brazil, no study has been carried out evaluating the presence of PAHs in equipment or absorbed by firefighters. Although some firefighters perform only few calls during the year (up to 10), as described in chapter 1 of this thesis, some professionals perform a greater number of fire combats, like fire instructors. These professionals end up coming into greater contact with toxic compounds, both directly and through cross-contamination.

Considering that, the aim of this research was to evaluate the presence of PAHs in Brazilian firefighters' personal protective equipment following training exercise of fire combat, as it were monitored exposures to firefighters in their occupational setting.

2. Objectives

The main objective of this chapter was to determine the presence and concentration of the USEPA’s 16 PAHs priority pollutants deposited on Brazilian firefighters’ personal protective equipment during a training exercise.

3. Materials and Methods

3.1. Chemicals and Reagents.

Polynuclear aromatic hydrocarbons analytical standard solution in acetonitrile were purchased from Sigma-Aldrich. The solution contained: acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene and pyrene. Acetonitrile, suitable for HPLC with a purity of greater than 99.9%, was purchased from the companies Exodo and JT Baker.

All glassware was washed with a neutral soap solution and rinsed with deionized water. Subsequently, rinses were carried out with the solvents ethanol (Synth), ethyl acetate (Synth) and dichloromethane (Merk) all of them were HPLC grade.

3.2. Equipment

- Analytical balance 250g, BEL Equipment, model M254Ai, precision of 0.0001 g;
- Ultrasound bath with heating, Solidsteel, model 1400, 10 L;
- Micropipette, Labtex, model MC902554, 200 - 1000 µL;
- Micropipette, BioPet, model CU0083320, 0.5 - 10 µL;
- Micropipette, Pegapet, model 000063531; 100-1000 µL;
- Micropipette, Pegapet, model 000062706; 10-100 µL;
- Amber vials with septum and cap, maximum capacity 2 mL;
- Amber feather bottle with screw cap and 30 mL stopper;
- 25 mL Volumetric Flask;
- 10 mL Volumetric Flask;
- Mass Spectrometer, Agilent, model 5973 inert;
- Gas Chromatograph, Agilent, model 6890N;
- Rxi®-1ms capillary column, with 100% methylpolysiloxane measuring 25 m X 0.20 mm X 0.33 µm, RESTEK;

3.3. Simulated fire scenario

For the training exercise, a simulated fire scenario was performed in a 40 feet shipping container (12 m x 2.35 m x 2.40 m), as shown in Figure 10a. The structure is divided in two parts: the observation chamber and the combustion chamber. Seven pieces of 10 mm plywood (2.20x1.10 m^2) and two pine pallets (1.2x0.8 m^2) were placed in the combustion chamber for fire ignition (Figure 10b).

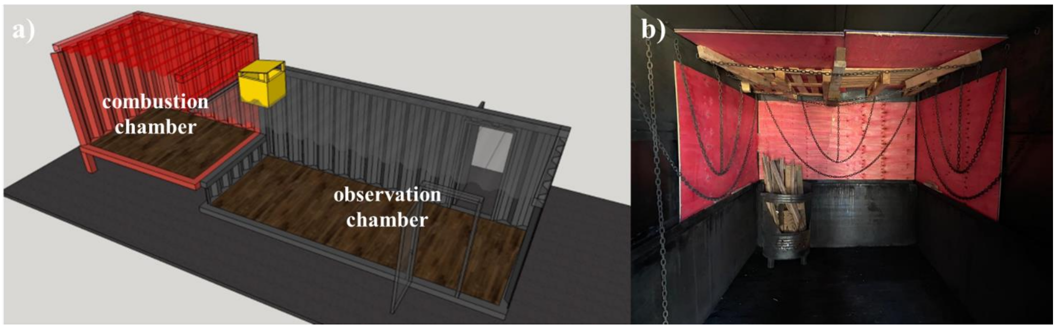


Figure 10. (a) Shipping container used during training exercise and **(b)** fire ignition assemble.

For the exercise, 10 firefighters and 2 instructors participated. They were positioned in pairs in the observation chamber, in line to carry out the fire attack appendix (Figure S1). The main objective of the exercise was to train branch techniques focused in cooling the smoke layer and suppressing hot spots of fire on instructor's command. During the exercise, the positions were switched so that all firefighters could attack the fire and practice the branch techniques. As the objective is to train branch techniques the instructors manage the scenario using the container openings (doors and chimney) to allow similar conditions of smoke, heat and fire for all firefighters. The training exercise took place for 25 minutes.

All firefighters were required to wear their own personal protective equipment as shown in appendix Figure S2 (without prior decontamination) according to Brazilian's firefighting instruction manual[84]. All participants gave consent before any procedure was performed.

3.4.Sample collection

Wipe sampling of firefighter were collected from 12 firefighters' personal protective equipment, in 4 different points: shoulder (P1), sleeve (P2), chest (P3) and gloves (in the palm) (P4), as shown in Figure 11.

The samples were collected using isopropyl alcohol 70% volume swabs (3.5x3.0 cm^2) in two different time: **prefire** (before-training exercise) and **postfire** (after-training exercise). The before-training exercise samples were collected in the left side of the PPE and the after-training exercise samples were collect in the right side. The sample were collected in an area of approximately 40 cm^2 (8 cm x 5 cm) in each point.

Figure 11. PPE wipe sampling in 4 different points: shoulder (P1), sleeve (P2), chest (P3) and gloves done prefire (before-training exercise) and postfire (after-training exercise).

Wipe sampling was done so that the integrity of the equipment was preserved, without the need to cut it to extract the contaminants. After the collection, the swabs were stored in amber flasks and stored in a freezer until extraction procedure.

3.5. Extraction procedure

Each swab was placed into a test tube with 5 mL of acetonitrile sonicated in an ultrasonic bath for 20 min at room temperature. The extract was stored, and another 5 mL of acetonitrile was added and sonicated for more 20 minutes, in order to ensure the complete extraction of contaminants. After extraction, the extracts were stored in amber flasks and stored in a freezer.

Also, an experiment was performed in order to determine the extraction efficiency. For that, pieces of fabric from the outer layer of the firefighters' turnout (composition of 58% para-aramid, 40% meta-aramid and 2% carbon) was cut into squares measuring 3x3 cm^2 and contaminated with a 0.0025 $mol.L^{-1}$ solution containing pyrene. 200 µL was spread on the fabric and air-dried. After that, pieces of contaminated fabrics were sampled with a swab and then extracted, according to the procedures described previously. This experiment was performed in triplicate.

3.6.Gas Chromatography-Mass Spectrometry analysis.

The presence and concentration of the 16 PAHs studied were by gas chromatograph (Agilent model 6890N) coupled with mass spectrometer (Agilent model 5973 inert). ASTM method 8270E[85] was used, with a Rxi®-1ms stationary phase capillary column, with 100% methylpolysiloxane of dimensions 25 mx 0.20 mm x 0.33 µm (RESTEK).

The injector temperature was maintained at 280°C, in Splitless mode with 1,3 µL injection. The column was maintained at a constant flow of helium at 0.5 mL/min. The chromatographic oven programming was: initial temperature of 40°C, held for 4 min, then heating at a rate of 10°C/min to 320 °C, keeping at this temperature for 2 min. The total time of analysis was 34 minutes. Solvent delay was used of 4,00 min and a gain factor of 20.

The GC/MS interface was maintained at 280°C, and the mass spectrometer was operated in scan mode in the scan range from 35 to 500 m/z, with HiSense.u. The mass spectra obtained were analyzed using the Chemstation Data Analysis software and the NIST Search software (version 2.3).

Quantification was conducted with external calibration curves with an analytical standard of 16 polynuclear aromatic hydrocarbons mix solution in acetonitrile. The analytical standard solution had a concentration of 10 µg each PAHs /ml, containing acenaphthene, acenaphthylene, anthracene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, fluorene, indeno[1,2,3-cd]pyrene, naphthalene, phenanthrene and pyrene.

All the data is available in appendix.

4. Results and Discussion

4.1.Calibration

The curves were constructed with a certified standard solution containing the 16 PAHs with the concentration of 10 μg/mL each component in acetonitrile. This certified standard solution was diluted in the in the concentration range described in Table 3.

Table 3. Standard solution used for the calibration process with GC/MS.

Standard solution (SS)	*Concentration (μg/mL)*
SS 1	0.20
SS 2	0.16
SS 3	0.12
SS 4	0.08
SS 5	0.04
SS 6	0.02

The analytical curves and residuals graphs for each compound are available in appendix. They presented coefficients of determination varying from 0.9504 to 0.9861. Despite not being an ideal value[86] (above 0.9900), it is an acceptable value, considering that the GC/MS method developed had as main purpose the detection of PAHs, instead of their quantification. This can be evidenced by the fact that the mass spectrometer was operated in scan mode, with HiSense.u.

Also, the ANOVA was performed, and all data are available in appendix. The F-test was performed showing that the regressions were adequate. Outliers were evaluated and the limit of detection (LOD) and limit of quantification (LOQ) for each of the 16 PAHs were obtained by the equation of the analytical curve, and the values obtained are described in appendix.

4.2. Extraction efficiency

The extraction efficiency test was performed using a piece of fabric from the outer layer of the firefighter's turnout contaminated with a known concentration of pyrene. This PAH was used due to availability and because it was used in other tests carried out in this thesis (chapter 3).

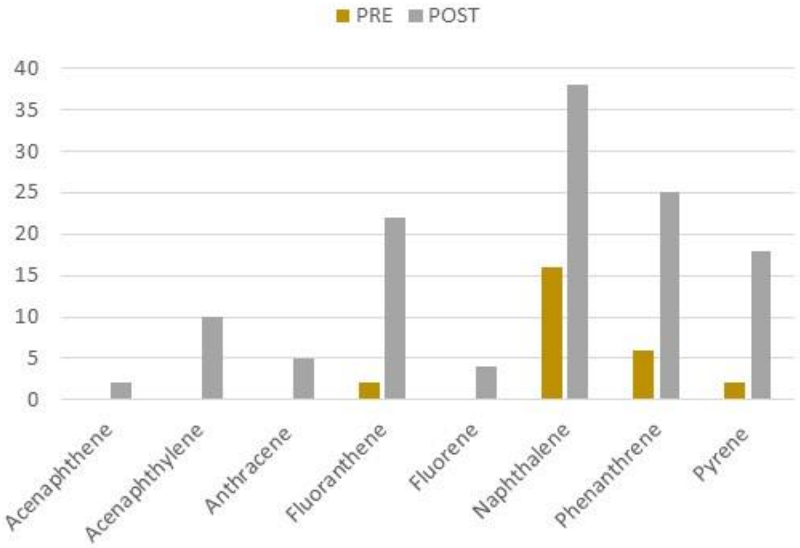
The test was performed in triplicate, and it was possible to recover 80% of the pyrene that was deposited on the fabric. The relative standard deviation obtained was ±14%.

4.3.Sample analysis

The main focus of the research is to determinate the presence of USEPA's 16 PAH priority pollutants in firefighters´ PPE, that can indicate the level of exposure of Brazilian firefighters during a training. This is the first study regarding the theme performed in a group of firefighters in Brazil, relating their occupational environment and the direct effect on their health.

Graph 21 show the results obtained prefire and postfire. In the samples analyzed by GC/MS, 8 of the 16 PAHs evaluated were detected in all samples: acenaphthene, acenaphthylene, anthracene, fluoranthene, fluorene, naphthalene, phenanthrene and pyrene. This is mainly due to rapid burning and exposition, as well as the temperature reached, which favored the formation of lower molecular weight PAHs. Higher temperature and longer periods favor the formation of higher molecular mass compounds[55,56].

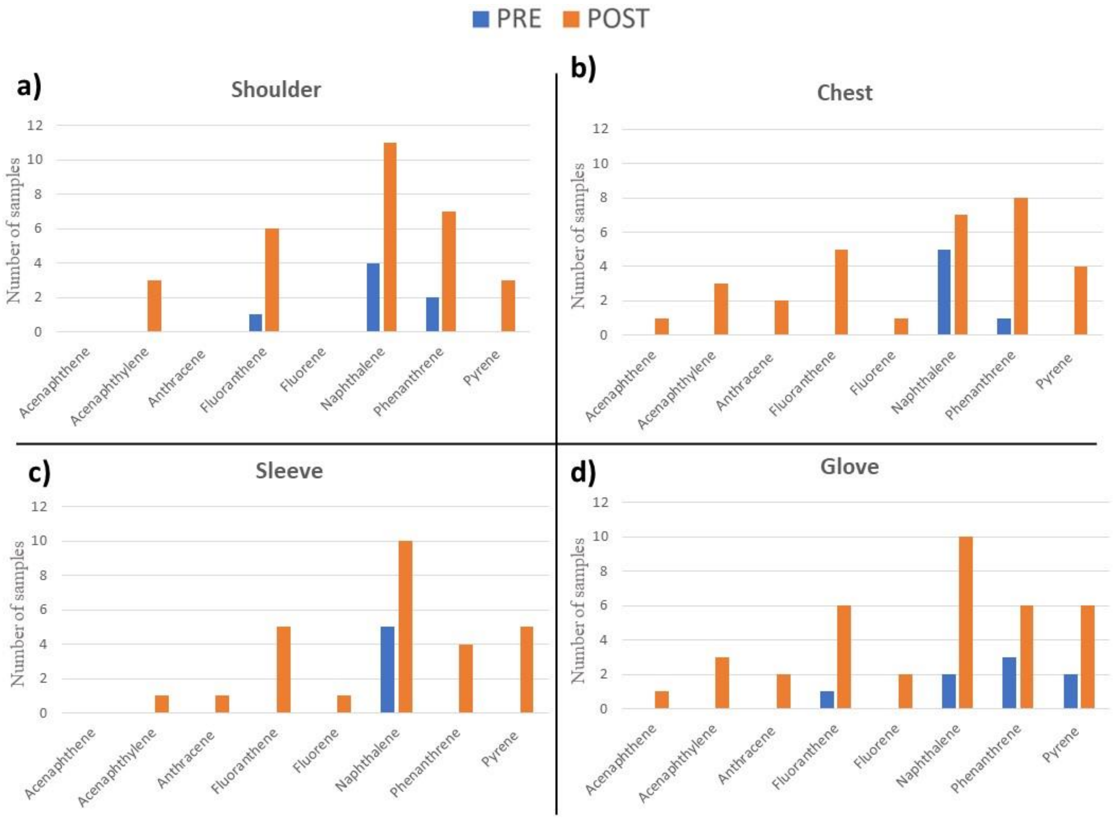
Before the training exercise (prefire), the most common PAH was naphthalene, which was found in 16 of the 48 samples tested (all firefighter and all points) (Graph 21). The second most found PAH was Phenanthrene, found in 6 samples. Other compounds found were fluoranthene and pyrene, however, in fewer samples and in lower concentration. In the samples after training (postfire), all 8 compounds were found. Again, the compounds naphthalene, phenanthrene, fluoranthene and pyrene were the most found (found in 38, 25, 22 and 18 samples, respectively),



Graph 21. Number of samples that presented PAHs pre and postfire.

Regarding to each sampling point (Graph 22), samples from chest, shoulder and sleeve showed a similar variety of PAHs deposited. For the samples collected at point P1 (shoulder, Graph 22a) before the exercise, the only PAHs found were naphthalene (found in 4 samples, phenanthrene (found in 2 samples) and fluoranthene (found in 1 samples). Other points, P2 (chest, Graph 22b) and P3 (sleeve, Graph 22c) presented a similar result. Postfire, samples collected in the chest and sleeve presented more positive results for the PAHs.

Samples collected in P4 (gloves, Graph 22d) presented a different result. After the training exercise, the quantity of samples that presented PAHs were higher, especially for PAHs different from naphthalene and phenanthrene. This difference can be associated to two facts. The first is because the firefighter touches more contaminated surfaces, unlike substances being deposited in the PPE. Second is the fact that the gloves are made with leather, a lower sheddability fabric[87]. With fabrics with higher sheddability, more compounds can penetrate through the fiber, making more difficult to extract it by swabbing. In leather, the compounds tend remain at the “surface”. Besides that, no greater difference was observed between collections points.



Graph 22. Number of samples that presented each PAHs collected in points **(a)** P1 (shoulder), **(b)** P2 (chest), **(c)** P3 (sleeve) and **(d)** P4 (glove) pre and postfire.

Analyzing each firefighter participant (Graph 23), the samples collected from firefighter nº 1 (FF1) presented either greater variety or quantity of deposited PAHs. During training, two instructors remained inside the container practically throughout all the exercise, they are: FF1 and FF7. Firefighter FF1 remained closer to the flames, while Firefighter FF7 remained closer to the exit. Therefore, it is reasonable that FF1 presented greater contamination when compared to the other participants. Prior to the exercise, only naphthalene was found in FF1 samples and after fighting the fire, all 8 PAHs were found, with a higher concentration. Regarding the firefighter FF7, as he remained further away from the flames, even though he remained in the container for a longer time, he presented a deposition pattern similar to the other participants.

Another participant that presented a different result was PFF 4 gloves samples. It was collected a higher number of compounds, when compared to others participants. Also, all 8 compounds were found in his/her sample. No specific reason for that was found, and it´s probably due to greater contact with a contaminated surface.

Graph 23. [PAH] (µg.mL^{-1}) for each firefighter participant (PFF 1 – PFF12) collected in points **(a)** P1 (shoulder), **(b)** P2 (chest), **(c)** P3 sleeve and **(d)** P4 (glove) pre and postfire.

The limit-concentration of PAHs is fixed in various legislations. In Brazil, CONAMA 357/2005[88] (*Conselho Nacional do Meio Ambiente)* determine limits of some of these compounds in water bodies. Values for fresh water (water with salinity equal to or less than 0.5% - intended for supply for human consumption where fishing or cultivation of organisms takes place, for intensive consumption purposes) are described in Table 4. The USEPA[89] also determine limits for these compounds in aqueous systems. These values range from 0.0012 μg.L^{-1} to 300 μg.L^{-1} and are related to the toxicity of each compound.

Specifically in the case of these compounds deposited in fabrics, some groups have carried out studies on the concentration of these compounds across the fabric area. Three studies describe this: Kirk and Logan [90], Fent *et al.*[64] and Stec *et al.*[82], and the values found are described in table 4. It is possible to note that the concentration of PAH varies, mainly due to the experimental methodology carried out. In the case of the collection carried out in our group, the concentration values of [PAHs] in ng.cm^{-2} can be seen in Graph 24. Although the experimental methodologies are different, there is a similarity between the results described in the literature by Kirk and Logan[90] and Fent *et al.* [64], varying in the range of 3.03 – 12.73 ng.cm^{-2} (average of Acenaphthene and Phenanthrene, respectively).

The Agency for Toxic Substances and Disease Registry (ATSDR) described in its report PAHs´ Minimal Risk Levels (MRLs – table 4) for professionals[93] . The MRL is an estimate of the daily human exposure to a hazardous substance that is likely to be without appreciable risk of adverse non-cancer health effects over a specified duration of exposure[91], in the case of the PAHs, the duration is 15-364 days. Considering that an 80 kg firefighter, during a day of work, the limit amounts of PAHs acenaphthene, anthracene, fluoranthene, fluorene and pyrene are: 48mg, 24 mg, 3.2 mg, 3.2mg and 2.4mg, respectively. Considering that after a fire combat, the PPE is contaminated with around 9.01 ng.cm^{-2} of pyrene (mean amount of pyrene at point P4 – Graph 24), it would be necessary for this firefighter to come into contact with an area larger than 270,000 cm^2 of contaminated PPE. Even if the values obtained in this thesis are lower than the MRL value, we must consider that there is a risk of contact with these materials. This occurs because there are different sources of contamination, besides, these results were obtained in a controlled situation, and in a real burning the concentrations of PAHs can increase. Also, we must still consider that not all PAH deposited in the firefighters' PPE were extracted, the value found shows the firefighters are in contact with a higher concentration than allowed in the norm, indicating a greater risk to the health of these professionals, especially the instructor.

Table 4. Concentration limits for 16 PAHs determined by CONAMA, USEPA, three works from the literature and OEKO-TEX.

Compound	*CONAMA 357/2005*^{a}	*USEPA*^{b}	*Kirk and Logan*^{c}	*Fent et al.*^{d}	*Stec et al.*^{e}	*MRL*^{f} *15-364 days*
Acenaphthene		70 µg.L^{-1}		0.46 ng.cm^{-2}		0.6mg/kg/day
Acenaphthylene			20 ng.cm^{-2}			
Anthracene		300 µg.L^{-1}	16.15 ng.cm^{-2}	0.38 ng.cm^{-2}		0.3mg/kg/day
Benzo(a)anthracene	0.018 µg.L^{-1}	0.0012 µg.L^{-1}	14.1 ng.cm^{-2}	0.90 ng.cm^{-2}	101.56 ng.cm^{-2}	
Benzo(a)pyrene	0.018 µg.L^{-1}	0.0012 µg.L^{-1}	11.175 ng.cm^{-2}	1.08 ng.cm^{-2}	114.15 ng.cm^{-2}	
Benzo(b)fluoranthene	0.018 µg.L^{-1}	0.0012 µg.L^{-1}	15 ng.cm^{-2}	0.75 ng.cm^{-2}	209.20 ng.cm^{-2}	
Benzo(ghi)perylene			10 ng.cm^{-2}	0.82 ng.cm^{-2}		
Benzo(k)fluoranthene	0.018 µg.L^{-1}	0.0012 µg.L^{-1}		0.39 ng.cm^{-2}	177.08 ng.cm^{-2}	
Chrysene	0.018 µg.L^{-1}	0.12 µg.L^{-1}	10.33 ng.cm^{-2}	0.70 ng.cm^{-2}	69.88 ng.cm^{-2}	
Dibenzo(a,h)anthracene	0.018 µg.L^{-1}	0.0012 µg.L^{-1}		1.91 ng.cm^{-2}		
Fluoranthene		20 µg.L^{-1}	37 ng.cm^{-2}	8.71 ng.cm^{-2}		0.04 mg/kg/day
Fluorene		50 µg.L^{-1}	14 ng.cm^{-2}	0.26 ng.cm^{-2}		0.04 mg/kg/day
Indeno(1,2,3-cd)pyrene	0.018 µg.L^{-1}	0.0012 µg.L^{-1}	11 ng.cm^{-2}	1.17 ng.cm^{-2}	74.65 ng.cm^{-2}	
Naphthalene				0.78 ng.cm^{-2}		
Phenanthrene			45 ng.cm^{-2}	2.58 ng.cm^{-2}		
Pyrene		20 µg.L^{-1}	40 ng.cm^{-2}	2.18 ng.cm^{-2}		0.03 mg/kg/day

[a] Values for fresh water (water with salinity equal to or less than 0.5% - intended for supply for human consumption where fishing or cultivation of organisms takes place, for intensive consumption purposes)[88].

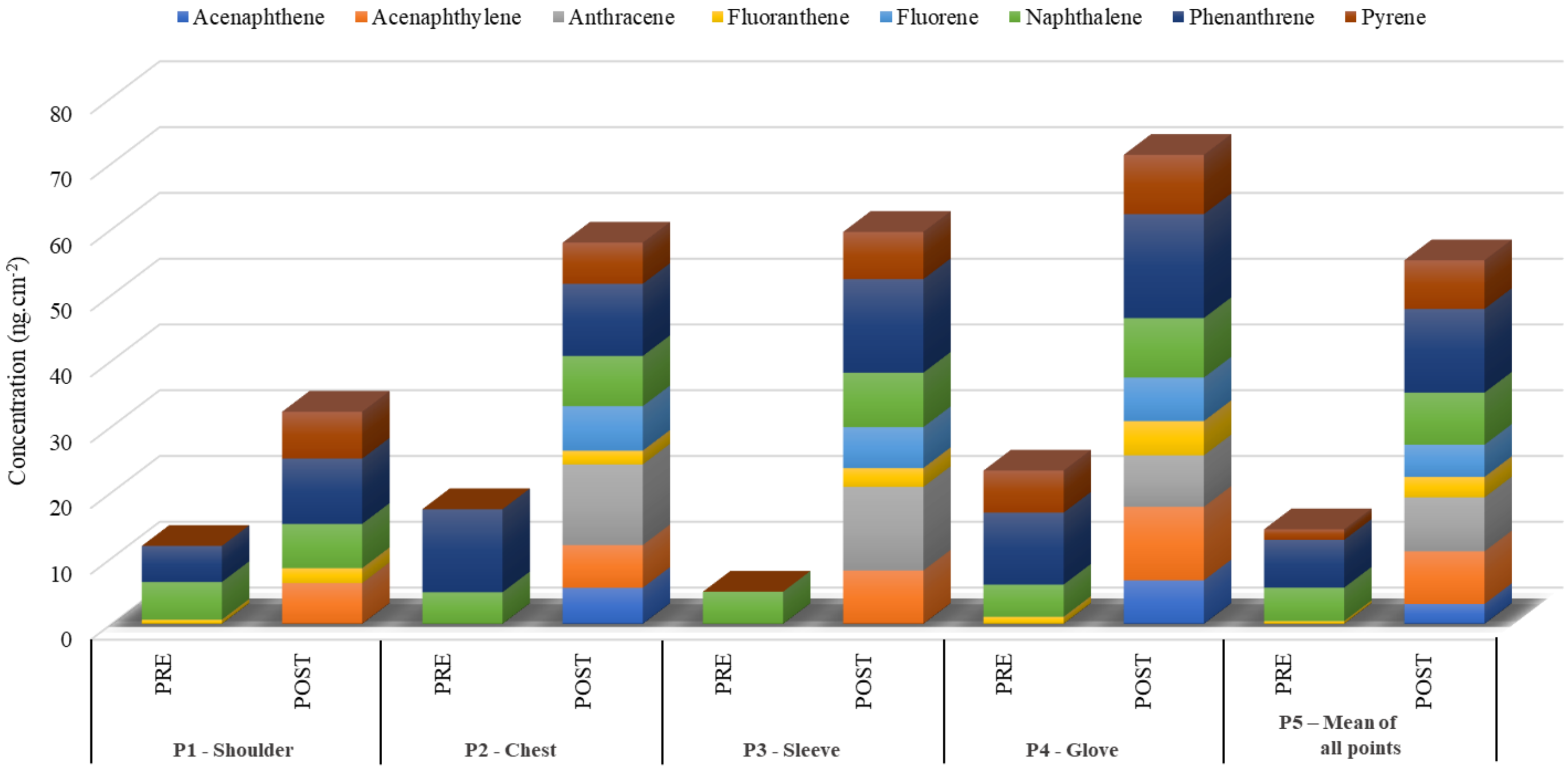
[b] National Recommended Water Quality Criteria - Human Health Criteria. Values for human health for the consumption of water + Organism[89].

[c] Kirk and Logan[90] concentration (ng/cm^2) of polycyclic aromatic hydrocarbons on structural firefighting ensembles of instructors during live fire training. Extraction of pieces of Nomex fabric attached to the ensemble.

[d] Fent *et al.*[64] Median levels of specific PAHs collected with wipes measured on hands of firefighters post-fire.

[e] Stec *et al.*[82] Mean of PAHs concentration (ng/cm^2) foin in PPE wipe samples, post-exposure, of four firefighters attending the training, collected in the gloves.

[f] Minimal Risk Levels (MRLs) – For Professionals described by Agency for Toxic Substances and Disease Registry (ATSDR)[93].



Graph 24. PAHs concentration (ng.cm^{-2}) found in P1, P2, P3, P4 and mean of all 4 points, pre and postfire.

5. Conclusion

The presence of Polycyclic Aromatic Compounds in firefighters is related to an increase in the risk for developing, lung, prostate, brain, kidney, and testicular cancers, mesothelioma, multiple myeloma, non-Hodgkin lymphoma. Because of the accumulation of these substances on firefighter turnout gear, they can be transferred to the skin of the firefighter. Considering that, in this chapter of the thesis, the presence of the 16 main PAHs monitored by the USEPA in firefighters PPE was evaluated before and after training exercise. Four sampling points were evaluated (chest, shoulder, sleeve and glove) in a 12-participants study. Samples were collected at two times, pre and post training. The extraction efficiency was evaluated and a value of 80±14% was obtained.

Ninety-six samples were analyzed by GC/MS to determine the presence and concentration of pollutants, of which 64 were positive. Of the 16 compounds evaluated, 8 were found, mainly in post-fire samples, but also in pre-fire. Naphthalene and phenanthrene were the most frequently found, presenting a concentration that ranged from 0.007 to 1.066 $\mu g.mL^{-1}$. When comparing the sampling points P1, P2 and P3, they all presented a similar pattern. Samples collected at gloves (P4) presented a higher and a larger variety of PAHs, as expected.

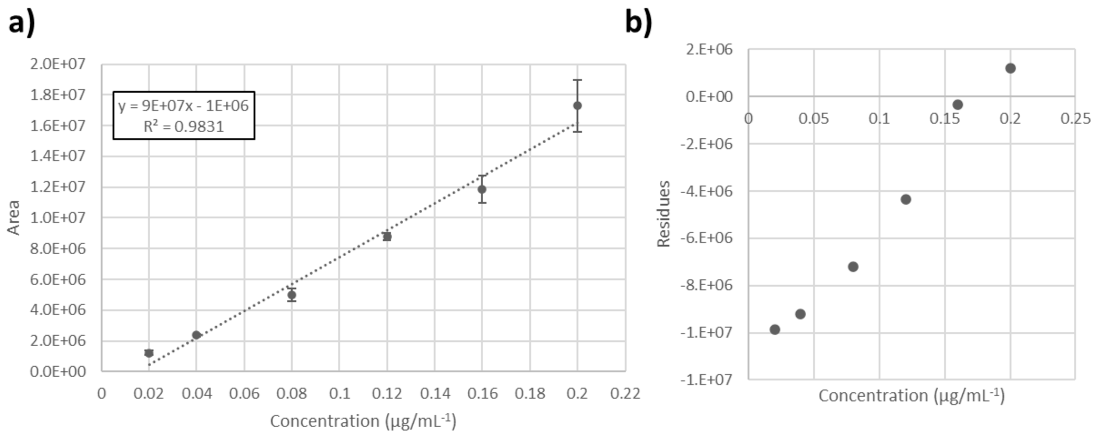
An important issue is the fact that fire instructors end up exposing themselves more frequently to these compounds as they conduct routinely fire trainings. This was evidenced in the present study by the participant FF1 (an instructor that was closer to the flames and remained inside the container practically throughout all the exercise) presented a greater/quantity variety of deposited PAHs when compared to other participants.

This study highlights the risk to which firefighters are exposed, even in relatively mild and controlled conditions such as training. Efforts should be taken to reduce this risk, in order to preserve the health of firefighters and also to reduce cross-contamination. With that in mind, the next chapter of this thesis will discuss techniques for decontaminating firefighter turnout gear.

6. Appendix

Figure S1. Firefighters position during the training exercise.

Figure S2. Firefighters' personal protective equipment used during the training exercise.



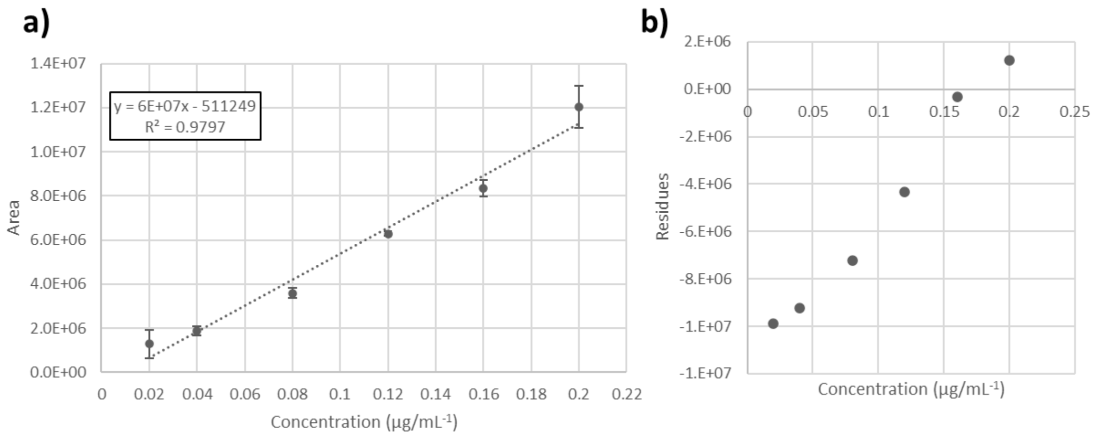
Graph S1. **(a)** Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte acenaphthene.

Table S1. GC/MS ANOVA table for the analyte acenaphthene.

Source	*Sum of Squares*	*Degrees of Freedom*	*Mean Squares*
Regression	1.85E+14	1	1.85E+14
Residual	3.18E+12	4	7.96E+11
Lack of fit	3.18E+12	4	7.96E+11
Total	1.88E+14	5	3.77E+13

Table S2. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte acenaphthene.

LOD	**LOQ**
0.0019	0.0062



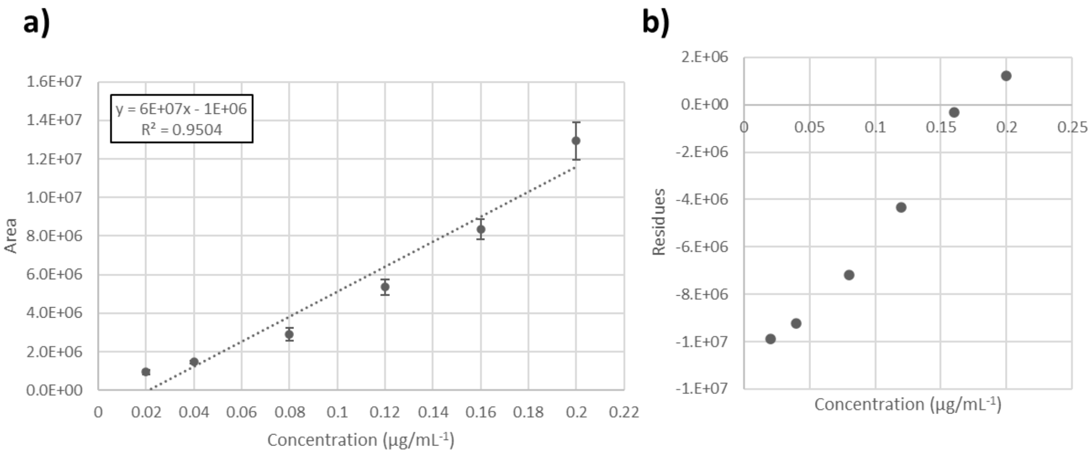
Graph S2. (a) Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte acenaphthylene.

Table S3. GC/MS ANOVA table for the analyte acenaphthylene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	8.43E+13	1	8.43E+13
Residual	1.75E+12	4	4.37E+11
Lack of fit	1.75E+12	4	4.37E+11
Total	8.60E+13	5	1.72E+13

Table S4. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte acenaphthylene.

LOD	**LOQ**
0.0020	0.0068



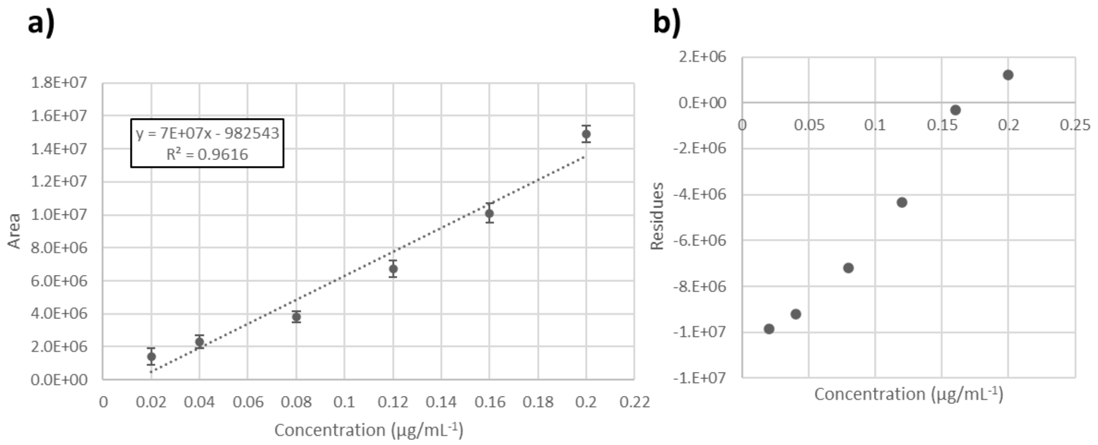
Graph S3. (a) Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte anthracene.

Table S5. GC/MS ANOVA table for the analyte anthracene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	1.02E+14	1	1.02E+14
Residual	5.30E+12	4	1.33E+12
Lack of fit	5.30E+12	4	1.33E+12
Total	1.07E+14	5	2.14E+13

Table S6. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte anthracene.

LOD	**LOQ**
0.0032	0.0108



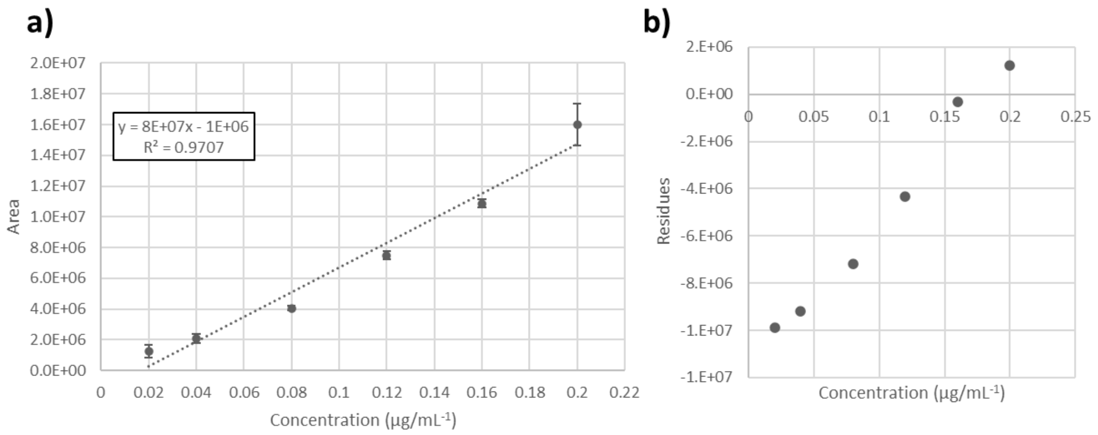
Graph S4. (a) Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte fluoranthene.

Table S7. GC/MS ANOVA table for the analyte fluoranthene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	1.29E+14	1	1.29E+14
Residual	5.17E+12	4	1.29E+12
Lack of fit	5.17E+12	4	1.29E+12
Total	1.34E+14	1	2.69E+13

Table S8. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte fluoranthene.

LOD	**LOQ**
0.0028	0.0095



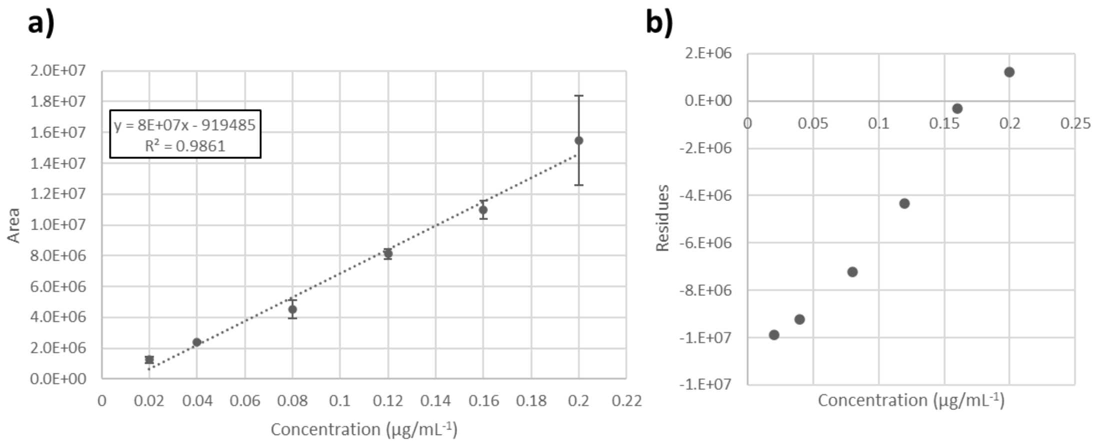
Graph S5. (a) Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte fluorene.

Table S9. GC/MS ANOVA table for the analyte fluorene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	1.57E+14	1	1.57E+14
Residual	4.75E+12	4	1.19E+12
Lack of fit	4.75E+12	4	1.19E+12
Total	1.62E+14	5	3.24E+13

Table S10. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte fluorene.

LOD	**LOQ**
0.0025	0.0082



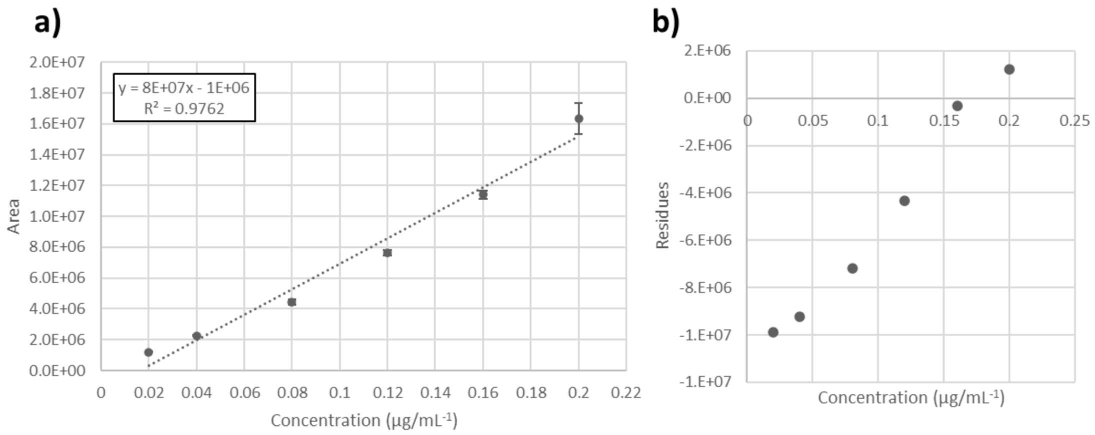
Graph S6. (a) Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte naphthalene.

Table S11. GC/MS ANOVA table for the analyte naphthalene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	1.47E+14	1	1.47E+14
Residual	2.07E+12	4	5.18E+11
Lack of fit	2.07E+12	4	5.18E+11
Total	1.49E+14	5	2.99E+13

Table S12. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte naphthalene.

LOD	**LOQ**
0.0017	0.0056



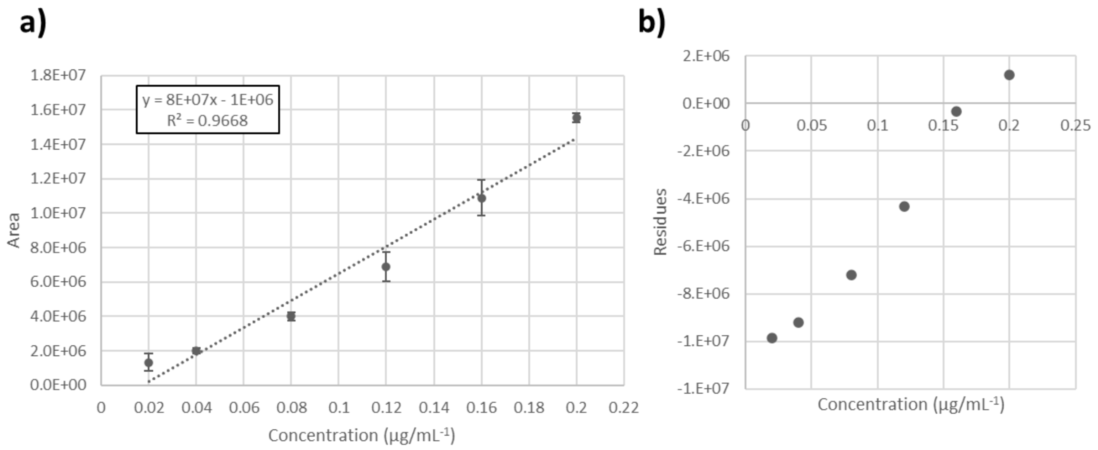
Graph S7. (a) Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte phenanthrene.

Table S13. GC/MS ANOVA table for the analyte phenanthrene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	1.65E+14	1	1.65E+14
Residual	4.04E+12	4	1.01E+12
Lack of fit	4.04E+12	4	1.01E+12
Total	1.69E+14	5	3.39E+13

Table S14. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte phenanthrene.

LOD	**LOQ**
0.0022	0.0074



Graph S8. (a) Analytical curve constructed using linear fit and **(b)** residues versus concentration for GC/MS analysis for the analyte pyrene.

Table S15. GC/MS ANOVA table for the analyte pyrene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	1.49E+14	1	1.49E+14
Residual	5.11E+12	4	1.28E+12
Lack of fit	5.11E+12	4	1.28E+12
Total	1.54E+14	5	3.08E+13

Table S16. Limits of detection (LOD) and quantification (LOQ), in µg.mL^{-1}, obtained by the analytical curves for the analyte pyrene.

LOD	**LOQ**
0.0026	0.0088

Table S17. PAHs concentration (μg.mL^{-1}) found in P1 (shoulder) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene																								
Acenaphthylene		**0.0308**				**0.0207**																**0.0230**		
Anthracene																								
Fluoranthene		**0.0160**		**0.0046**		**0.0117**							**0.0026**			**0.0054**						**0.0100**		**0.0067**
Fluorene																								
Naphthalene	**0.0306**	**0.0550**				**0.0233**		**0.0257**	**0.0146**	**0.0164**		**0.0317**		**0.0228**	**0.0242**	**0.0157**	**0.0223**	**0.0351**		**0.0222**		**0.0242**		**0.0243**
Phenanthrene		**0.0724**		**0.0245**				**0.0357**						**0.0310**	**0.0246**	**0.0254**						**0.0467**	**0.0193**	**0.0421**
Pyrene		**0.0371**												**0.0224**						**0.0260**				

Table S18. PAHs concentration (μg.mL^{-1}) found in P2 (chest) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene		**0.0220**																						
Acenaphthylene		**0.0410**				**0.0254**																**0.0115**		
Anthracene		**0.0468**						**0.0513**																
Fluoranthene		**0.0223**												**0.0048**						**0.0058**		**0.0045**		**0.0046**
Fluorene		**0.0271**																						
Naphthalene		**0.0586**						**0.0134**	**0.0127**		**0.0137**	**0.0237**		**0.0257**	**0.0182**		**0.0262**	**0.0550**	**0.0254**	**0.0201**				**0.0172**
Phenanthrene		**0.0838**				**0.0398**								**0.0359**	**0.0505**	**0.0237**		**0.0366**		**0.0404**		**0.0458**		**0.0450**
Pyrene		**0.0313**				**0.0226**		**0.0200**						**0.0262**										

Table S19. PAHs concentration (µg.mL^{-1}) found in P3 (sleeve) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene																								
Acenaphthylene		**0.0325**																						
Anthracene		**0.0508**																						
Fluoranthene		**0.0208**						**0.0068**						**0.0064**								**0.0109**		**0.0127**
Fluorene		**0.0249**																						
Naphthalene	**0.0297**	**0.1066**				**0.0199**	**0.0138**	**0.0232**	**0.0134**	**0.0396**	**0.0204**	**0.0202**		**0.0272**		**0.0210**		**0.0312**			**0.0205**	**0.0199**		**0.0223**
Phenanthrene		**0.1041**				**0.0433**		**0.0406**						**0.0396**										
Pyrene		**0.0417**				**0.0222**		**0.0253**												**0.0284**				**0.0259**

Table S20. PAHs concentration (µg.mL^{-1}) found in P4 (glove) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene								**0.0265**																
Acenaphthylene				**0.0243**				**0.0837**								**0.0261**								
Anthracene				**0.0229**				**0.0397**																
Fluoranthene				**0.0096**		**0.0603**		**0.0192**			**0.0007**			**0.0097**		**0.0187**					**0.0079**	**0.0079**		
Fluorene				**0.0238**				**0.0291**																
Naphthalene		**0.0178**		**0.0210**				**0.1334**		**0.0254**	**0.0132**	**0.0246**		**0.0263**		**0.0266**	**0.0204**	**0.0340**			**0.0253**	**0.0253**		**0.0278**
Phenanthrene		**0.0589**		**0.0517**				**0.1135**					**0.0480**		**0.0431**	**0.0616**	**0.0300**	**0.0395**			**0.0539**	**0.0539**		
Pyrene		**0.0324**		**0.0238**				**0.0476**			**0.0188**		**0.0282**	**0.0276**		**0.0489**					**0.0297**			

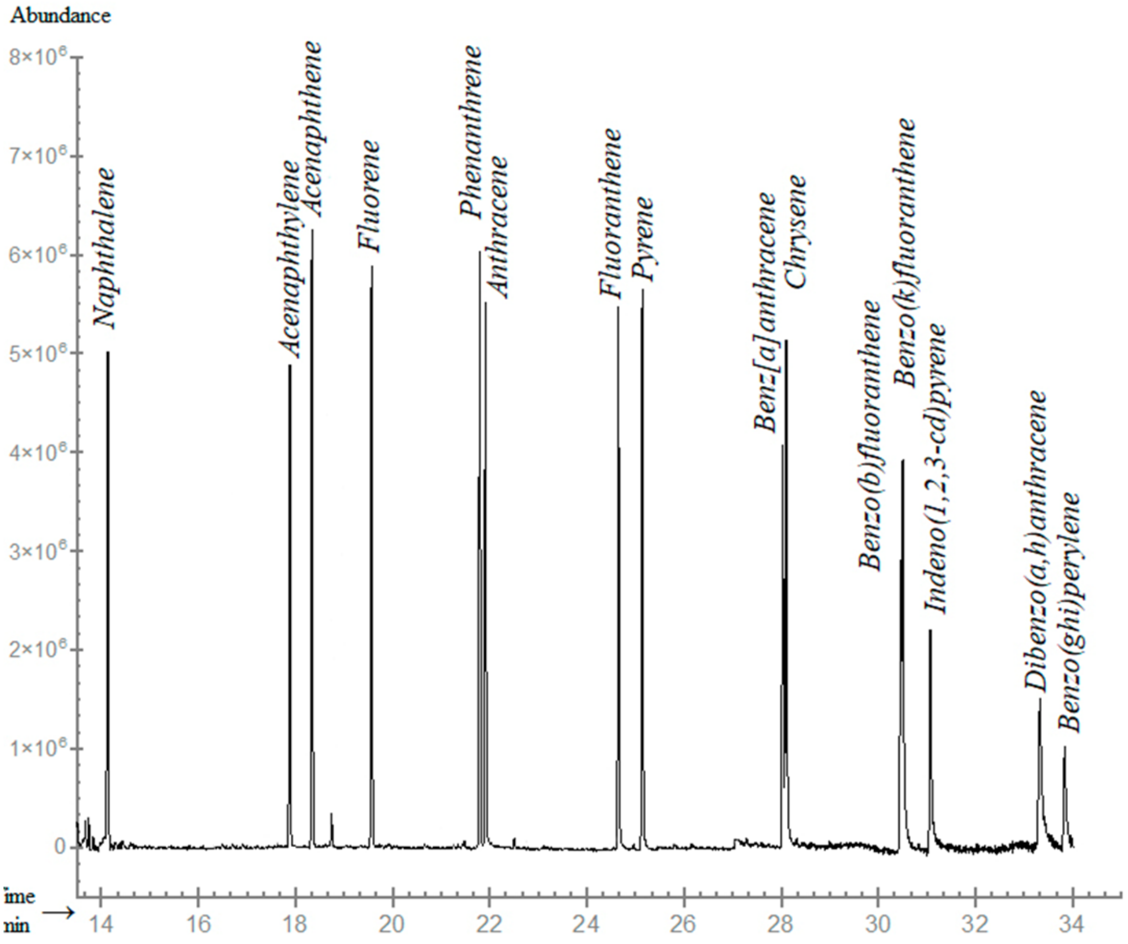


Figure S3. Chromatogram obtained by GC/MS of a 16 PAH mixture.

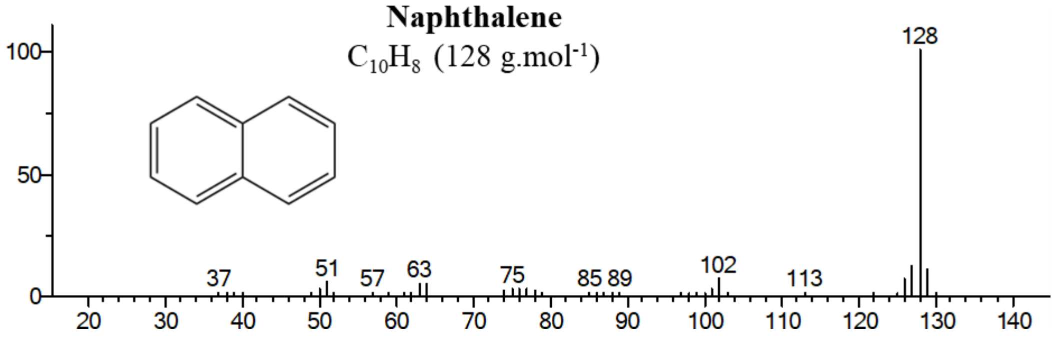


Figure S4. Mass spectrum of the naphthalene (RT 14.142 min) obtained by GC/MS.

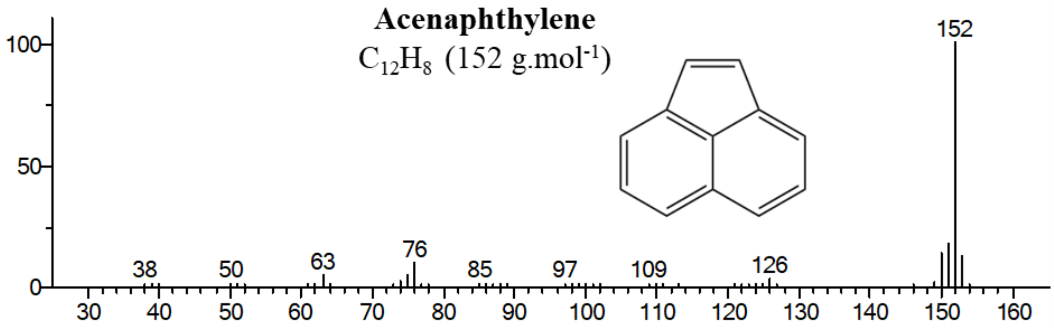


Figure S5. Mass spectrum of the acenaphthylene (RT 17.880 min) obtained by GC/MS.

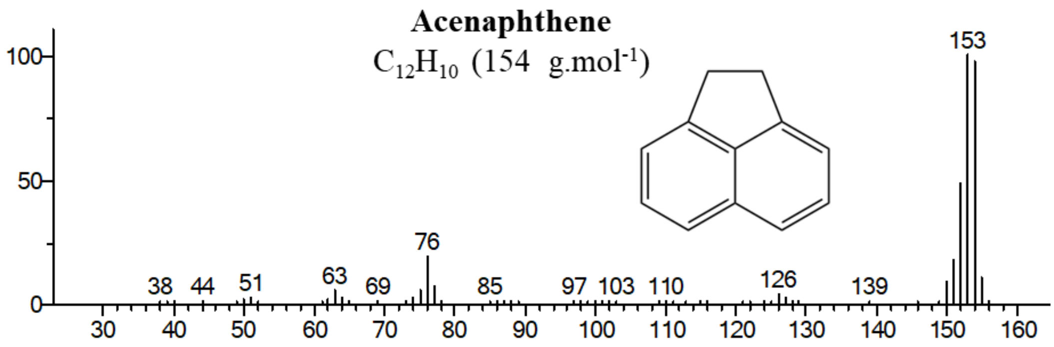


Figure S6. Mass spectrum of the acenaphthene (RT 18.346 min) obtained by GC/MS.

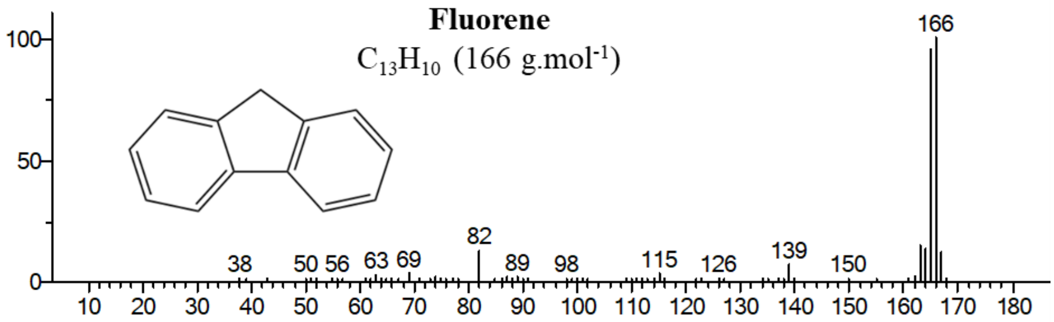


Figure S7. Mass spectrum of the fluorene (RT 19.573min) obtained by GC/MS.

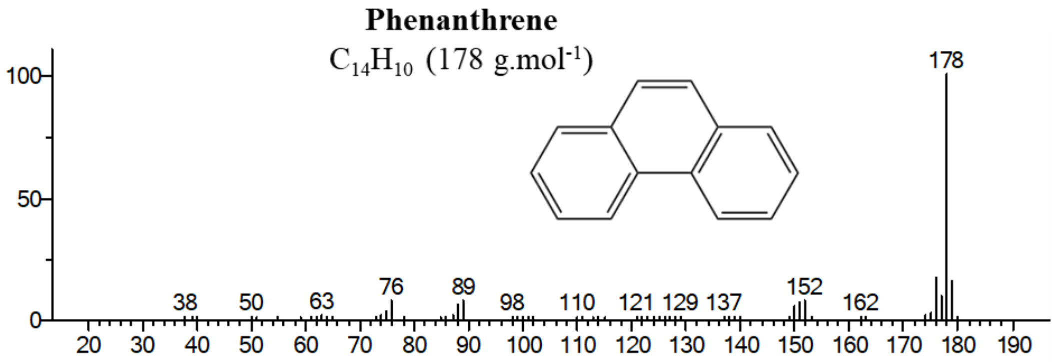


Figure S8. Mass spectrum of the phenanthrene (RT 21.796 min) obtained by GC/MS.

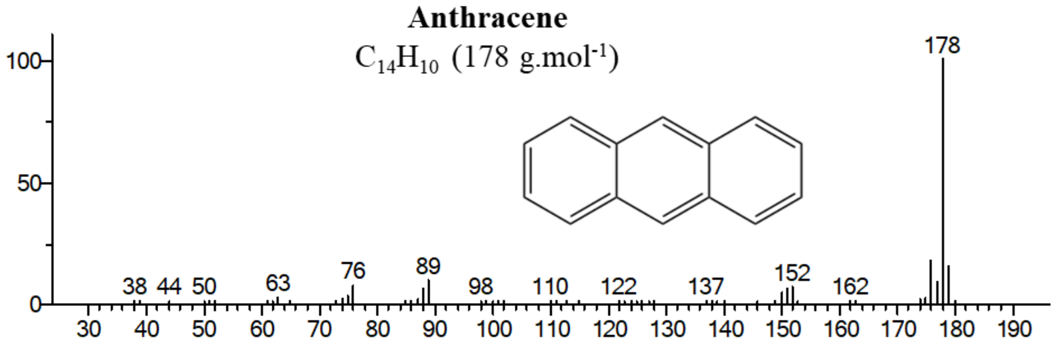


Figure S9. Mass spectrum of the anthracene (RT 21.918 min) obtained by GC/MS.

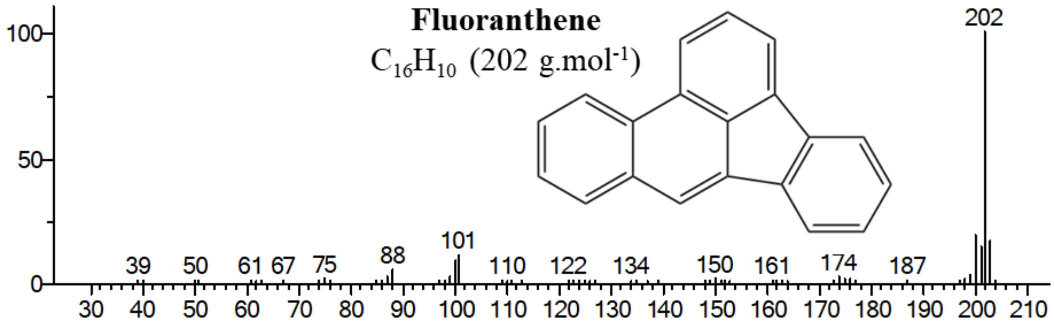


Figure S10. Mass spectrum of the fluoranthene (RT 24.657 min) obtained by GC/MS.

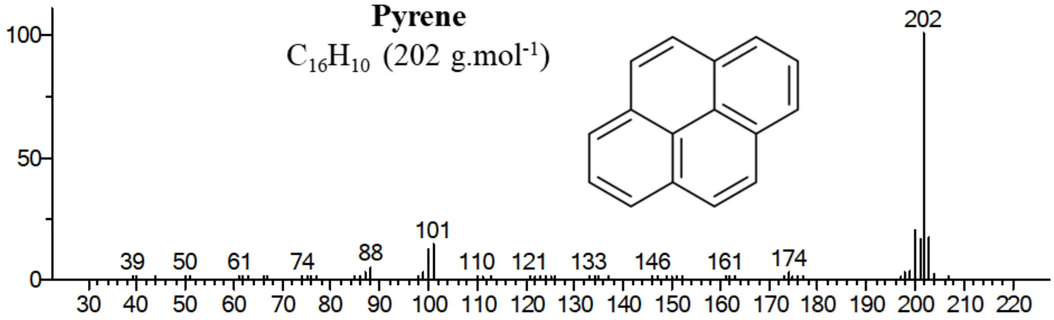


Figure S11. Mass spectrum of the pyrene (RT 25.145min) obtained by GC/MS.

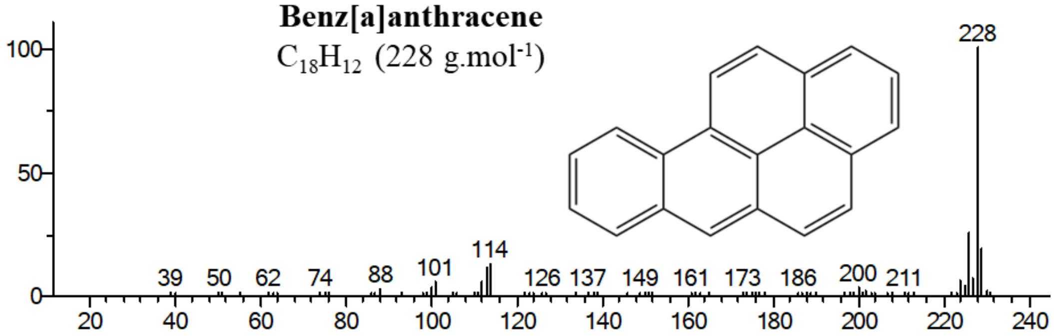


Figure S12. Mass spectrum of the benzo(a)anthracene (RT 28.038 min) obtained by GC/MS.

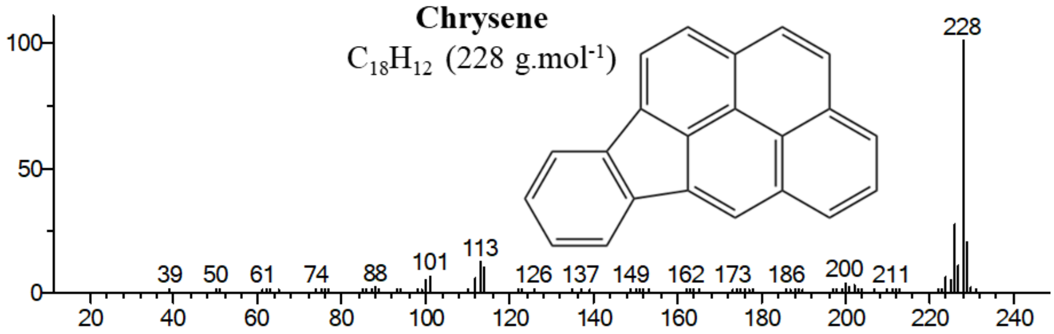


Figure S13. Mass spectrum of the chrysene (RT 28.041 min) obtained by GC/MS.

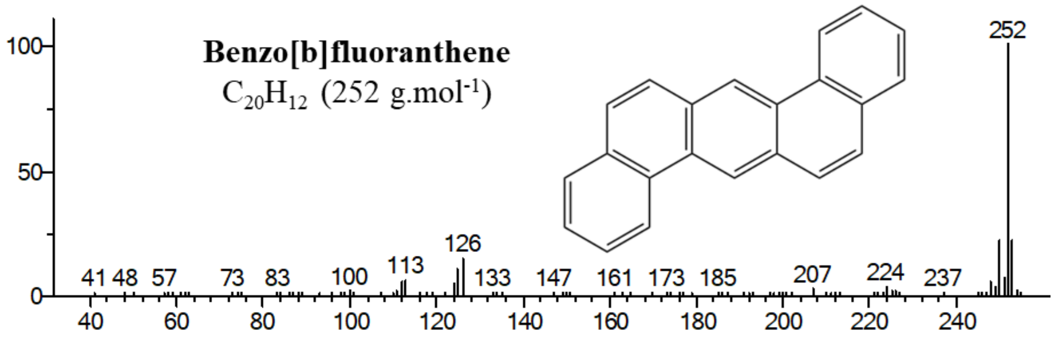


Figure S14. Mass spectrum of the benzo(b)fluoranthene (RT 30.456 min) obtained by GC/MS.

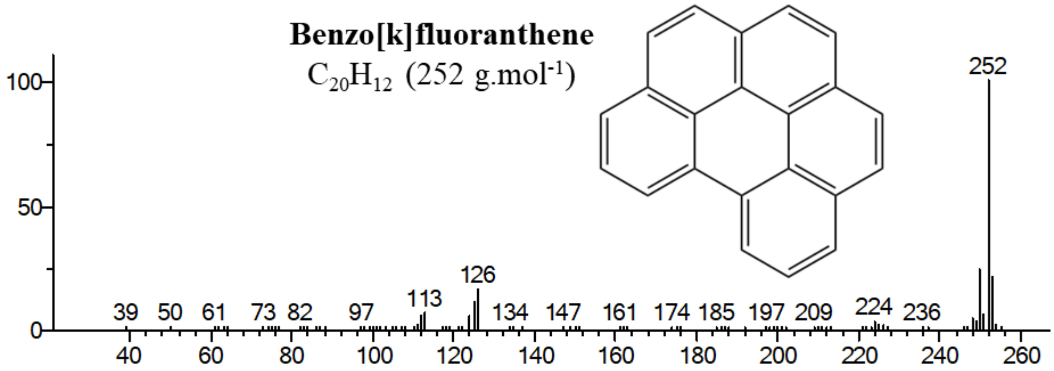


Figure S15. Mass spectrum of the benzo(k)fluoranthene (RT 30.503 min) obtained by GC/MS.

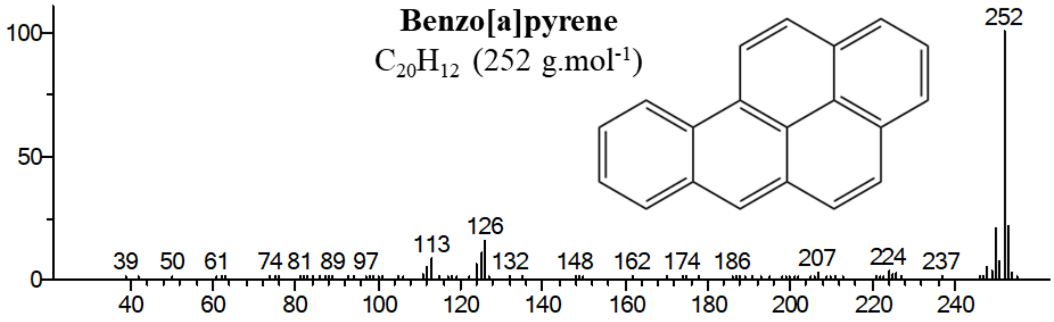


Figure S16. Mass spectrum of the benzo(a)pyrene (RT 31.076 min) obtained by GC/MS.

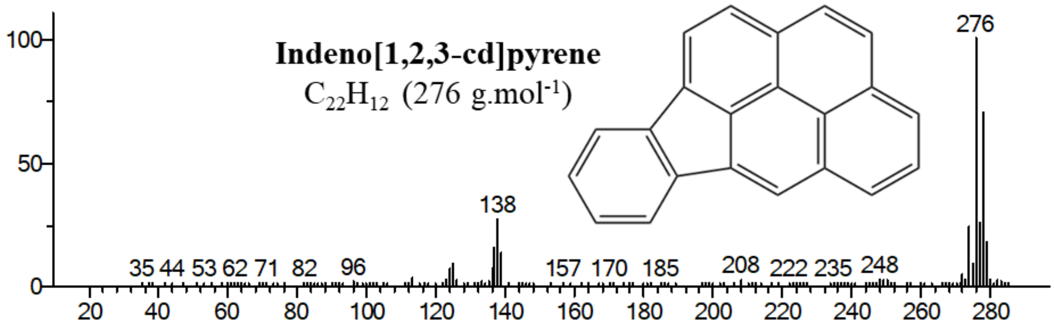


Figure S17. Mass spectrum of the indeno(1,2,3-cd)pyrene (RT 33.324 min) obtained by GC/MS.

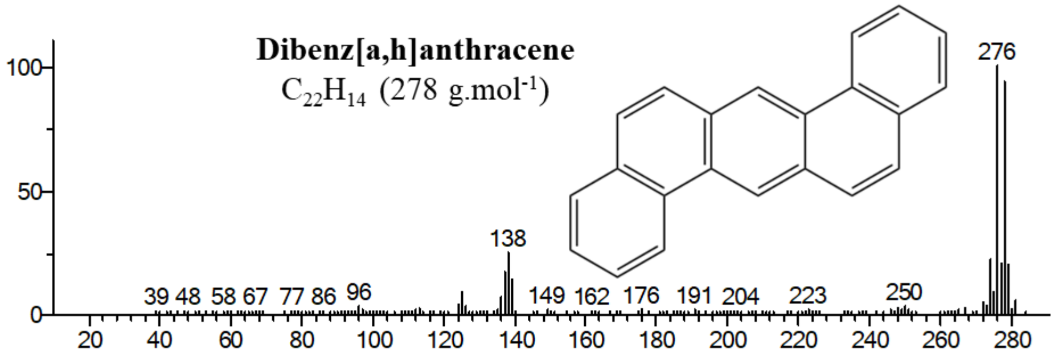


Figure S18. Mass spectrum of the dibenzo(a,h)anthracene (RT 33.336 min) obtained by GC/MS.

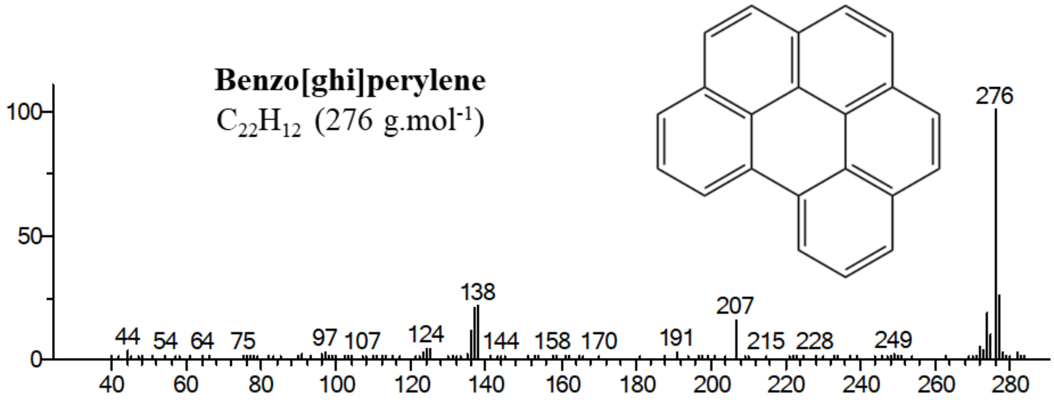


Figure S19. Mass spectrum of the benzo(ghi)perylene (RT 33.8462 min) obtained by GC/MS

Table S21. PAHs concentration (ng.cm^{-2}) found in P1, P2, P3, P4 and mean of all 4 points pre and postfire.

	P1		*P2*		*P3*		*P4*		*Mean*	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene	0.00	0.00	0.00	5.49	0.00	0.00	0.00	6.62	0.00	3.03
Acenaphthylene	0.00	6.21	0.00	6.49	0.00	8.12	0.00	11.18	0.00	8.00
Anthracene	0.00	0.00	0.00	12.26	0.00	12.70	0.00	7.82	0.00	8.20
Fluoranthene	0.64	2.26	0.00	2.10	0.00	2.88	1.07	5.22	0.43	3.11
Fluorene	0.00	0.00	0.00	6.76	0.00	6.22	0.00	6.60	0.00	4.90
Naphthalene	5.73	6.73	4.81	7.63	4.89	8.27	4.91	9.05	5.08	7.92
Phenanthrene	5.48	9.92	12.62	10.97	0.00	14.23	10.94	15.80	7.26	12.73
Pyrene	0.00	7.12	0.00	6.26	0.00	7.18	6.39	9.01	1.60	7.39

Table S22. PAHs concentration (ng.cm^{-2}) found in P1 (shoulder) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene																								
Acenaphthylene		**7.71**				**5.17**																**5.75**		
Anthracene																								
Fluoranthene		**3.99**		**1.14**		**2.93**							**0.64**			**1.35**						**2.51**		**1.67**
Fluorene																								
Naphthalene	**7.65**	**13.74**				**5.83**		**6.41**	**3.65**	**4.11**		**7.92**		**5.71**	**6.06**	**3.92**	**5.57**	**8.78**		**5.54**		**6.06**		**6.07**
Phenanthrene		**18.10**		**6.13**				**8.93**						**7.74**	**6.15**	**6.35**						**11.69**	**4.81**	**10.52**
Pyrene		**9.27**												**5.59**						**6.50**				

Table S23. PAHs concentration (ng.cm^{-2}) found in P2 (chest) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene		**5.49**																						
Acenaphthylene		**10.25**				**6.34**																**2.88**		
Anthracene		**11.69**						**12.83**																
Fluoranthene		**5.57**												**0.00**						**1.45**		**1.12**		**1.15**
Fluorene		**6.76**																						
Naphthalene		**14.64**						**3.34**	**3.17**		**3.41**	**5.94**		**6.41**	**4.56**		**6.55**	**13.75**	**6.35**	**5.02**				**4.30**
Phenanthrene		**20.95**				**9.96**								**8.97**	**12.62**	**5.92**		**9.15**		**10.11**		**11.45**		**11.25**
Pyrene		**7.83**				**5.65**		**5.00**						**6.54**										

Table S24. PAHs concentration (ng.cm^{-2}) found in P3 (sleeve) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene																								
Acenaphthylene		**8.12**																						
Anthracene		**12.70**																						
Fluoranthene		**5.21**						**1.70**						**1.59**								**2.72**		**3.16**
Fluorene		**6.22**																						
Naphthalene	**7.43**	**26.65**				**4.98**	**3.46**	**5.80**	**3.35**	**9.90**	**5.09**	**5.04**		**6.79**		**5.24**		**7.80**			**5.12**	**4.96**		**5.57**
Phenanthrene		**26.02**				**10.83**		**10.15**						**9.90**										
Pyrene		**10.43**				**5.54**		**6.33**												**7.10**				**6.49**

Table S25. PAHs concentration (ng.cm^{-2}) found in P4 (glove) pre and postfire of each participant.

	1		2		3		4		5		6		7		8		9		10		11		12	
	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST	PRE	POST
Acenaphthene								**6.62**																
Acenaphthylene				**6.06**				**20.93**								**6.53**								
Anthracene				**5.72**				**9.92**																
Fluoranthene				**2.39**		**15.06**		**4.80**			**0.18**			**2.43**		**4.67**					**1.97**	**1.97**		
Fluorene				**5.94**				**7.26**																
Naphthalene		**4.44**		**5.25**				**33.35**		**6.35**	**3.30**	**6.14**		**6.56**		**6.65**	**5.10**	**8.50**			**6.32**	**6.32**		**6.96**
Phenanthrene		**14.74**		**12.93**				**28.39**					**11.99**		**10.78**	**15.41**	**7.51**	**9.88**			**13.47**	**13.47**		
Pyrene		**8.10**		**5.95**				**11.89**			**4.70**		**7.05**	**6.89**		**12.23**					**7.44**			

CHAPTER 3

PROXIMITY FIREFIGHTING PROTECTIVE CLOTHING DESCONTAMINATION OF POLYCYCLIC AROMATIC HYDROCARBONS

1. Theoretical reference

1.1. Decontamination process

Cross contamination is one of the main exposure route of firefighters after the fire attack. These pollutants, particularly PAHs that are less volatile, can be transferred from personal protective equipment or combat scene surfaces to firefighter, vehicles, and institutional facilities[82,90,94]. In addition, storage in private places (cars, indoors and shared closets) can lead to the exposure of other people who share the spaces [94].Considering this fact, it is extremely important to carry out a decontamination procedure not only for the PFPC, as well as for the other PPEs.

Several studies were carried out with the aim of developing a safe and effective method of decontamination of the turnout gear. Most studies had explored physical methods of decontamination, such as, laundering, brushing process and using compressed air. For instance, Fent *et al.*[64] evaluated the efficiency of these methods soon after combat. Brushing PFPC with soap solution showed an 85% reduction in PAHs. With dry brushing it was possible to reduce by 23% and the use of compressed air promoted the worst result, removing only 1.9% of PAHs.

Decontamination by brushing is a simple technique, which is usually performed at the combat scene itself. For this, a solution of neutral soap is poured with the aid of a spray bottle. Then the suit is scrubbed with a plastic bristle brush and rinsed quickly with pressurized water, preventing water from penetrating the last layer of the approach suit. This procedure was described by Fent *et al.*[64] and is also the one applied by CBMDF firefighters (figure 12).

Calvillo *et al.*[95] evaluated the decontamination with pressurized water only, performed immediately after the combat and can be performed in the scene itself. It was not efficient to remove PAH. In fact, there was an increase in the concentration in some suits, suggesting that, in addition to not removing the compounds, the method would promote cross-contamination.

Figure 12. Decontamination process by brushing carried out in training by CBMDF firefighters.

The NFPA, after a series of scientific studies, created a standard with guidelines for an adequate method of cleaning PFPC, which consists in a laundering process. The NFPA 1851[75] standard, in section 7.3 Advanced Cleaning, describes all the cleaning procedures, such as the type of machine that must be used, type of detergent, washing and drying cycles, among others. This is the most used one and is usually performed a few times, about 2 times a year[64]. The minimum number of washes is also determined by NFPA 1851[75].

Despite removing PAHs from the fabrics of the outer layer of firefighter suits, the laundering process promotes a reduction in the physical and thermal properties of the fabrics. Studies[76–78] show that after various laundering cycles using the NFPA 1851 decon, it is possible to identify wear and damage to items. The PFPC is a high-cost PPE, and in a bid carried out by the CBMDF in 2017, the purchase value of a unit was €1,419.58[96], equivalent to R$ 8703.54 today (conversion from €1 to R$ $6.13). Considering this high value, turnout conservation is extremely important, so that the decontamination method must preserve the thermal and physical properties of the fibers.

In addition to the damage caused to the fabric fibers of the turnout, washing contaminated garments can promote cross-contamination of other garments inside the machine, as observed by Mayer *et al.*[74] They observed that washing promoted a reduction of around 85-90% of PAH contamination in hoods after the washing process. However, there was an increase in the concentration of contaminants in clean hoods, indicating cross-contamination.

In USA, the main standard used is the NFPA 1851[75] standard. In the European Union, the ISO standard (ISO 23616) is still being discussed. The ISO standard aims to determine methods for cleaning, inspecting, and repairing personal protective equipment and is still under development. In Brazil, there is no guidance on procedures for laundering and decontaminating the turnout. In the CBMDF, the washing guidelines provided by Texport, the company responsible for manufacturing the PFPC of the corporation, table 5, are followed.

In a monograph written by Nunes in 2021[18], a study of the advanced cleaning method described in the NFPA 1851[75] standard was presented, with the presentation of a draft standard operating procedure in order to guide the CBMDF itself on how to perform the cleaning of the turnout.

Table 5. Washing guidelines used in CBMDF [18].

General Cleaning Instructions	• Wash clothing separately; • Remove unfixed accessories; • Latches must be closed; • Close the jacket, cover the velcro fasteners with soft tape and turn the jacket inside out (lining for outside) • Pre-treat extremely dirty parts; • Use delicate laundry detergents (without bleachers, no softeners, do not use concentrates); • Water pH should be between 8 and 9; • Do not use fabric softeners; • Do not pack when wet; • Ironing with temperature adjusted according to label; • In case of chemical cleaning, do not use tonics; • To avoid damage after industrial cleaning, • A previous test cleaning is recommended; • In case of need to restore repellency to liquids and chemicals net by virtue of certain rules, the manufacturer will provide more information about waterproofing intervals after cleaning; • Do not use bleaches.
Maximum water temperature	60°C
Ironing	Iron at 150°C. Do not iron reflector strips.
Centrifugation	Normal.
Dying	It is possible to dry in the dryer, taking care to close the jacket, cover the velcro with soft tape and turn the jacket inside out (lining facing out).
Storage	Stored protected from light in a clean and dry place; must be protected from sunlight

Soure: Nunes, B. M. de A., 2021[18].

These physical decontamination technique aren´t able to fully remove PAH[64,74,95,97], and in some cases, it promotes a reduction in the physical and thermal properties of fabrics[76–78].

Another alternative is the chemical decontamination, as performed by Lucena *et al.*[98], that evaluated the ozonolysis of model PAHs (pyrene and 9-methylanthracene) in pieces of impregnated turnout gear using ozone chamber. After treatment for 60 minutes, it was possible to degrade 14±6% for pyrene and 36±3% for 9-methylanthracene. Despite being able to decontaminate a part of the PAHs, the result was unsatisfactory (due to the small degradation percentage.

Ozonolysis consists of the use of Ozone (O_3) to promote the degradation of pollutants. Two mechanisms can occur: direct ozonolysis (eq. 4) and indirect ozonolysis, which occurs in an alkaline medium and there is the formation of the OH• radical (eq.5)[99,100]. The efficiency of ozonolysis can be increased with the addition of H_2O_2 or UV radiation. The O_3/UV, O_3/H_2O_2 and $O_3/UV/H_2O_2$ systems are described in equations 6-8, respectively. The technique using O_3/H_2O_2 is more suitable for organic compounds that do not absorb in the UV[99] region.

$$O_3 + PAH \longrightarrow PAH_{oxi} \tag{4}$$

$$O_3 + OH^- \longrightarrow O_3{\bullet}^- + OH{\bullet} \tag{5}$$

$$O_3 + H_2O \xrightarrow{h\nu} 2OH{\bullet} + O_2 \tag{6}$$

$$2O_3 + H_2O_2 \longrightarrow 2OH{\bullet} + 3O_2 \tag{7}$$

$$2O_3 + H_2O_2 \xrightarrow{h\nu} 2OH{\bullet} + 3O_2 \tag{8}$$

Another issue that must be considered when using ozone is its toxicity. Exposure to the O_3 molecule can cause several effects to the respiratory system, with an inflammatory effect, changes in lung capacity, resistance to flow, epithelial permeability and reactivity to bronchoactive challenges[101]. At high concentrations and under chronicle exposure, a constriction of the airways pathways can occur, resulting in reduced flow of inhaled air[102]. Therefore, the use of ozone decontamination chambers can harm the users, who end up being exposed to the gas.

Considering that, searching for solutions for the decontamination of suits that do not damage fibers remains as an open issue. The use of advanced oxidative processes other than ozonolysis can be an alternative to the classic decontamination methods already applied by firefighters.

1.2.AOPs

Advanced Oxidative Processes (AOPs) are a series of techniques involveing production of free radicals that are able to oxidize organic compounds, resulting in lighter or more biodegradable compounds or, even, promoting complete mineralization [103–105]. These techniques are widely used in the treatment of effluents[106–114] and soils[115–120] contaminated with highly recalcitrant organic pollutants such as phenols, organochlorines and polycyclic aromatic hydrocarbons.

AOPs consists of the reaction between the pollutant and a radical (oxidizing agent) that can attack organic compounds. The hydroxyl radical is one of the most effective and most used oxidizing agents[106], as demonstrated by its high reduction potential (Table 6). Three initial mechanisms can occur during degradation by an advanced oxidative process: hydrogen atom abstraction, electron transfer and electrophilic addition[103]. The mechanisms are described in Figure 13.

Table 6. Standard reduction potentials of oxidizing agents used in AOPs [106].

Oxidizing Agent	**E^o_{red} (V)**
Fluorine	3,06
Hydroxyl Radical	2,8
Oxygen (atonic)	2,42
Ozone	2,08
Hydrogen peroxide	1,78
Hypochlorite	1,49
Chlorine	1,36
Chlorine dioxide	1,27

Souce: Tchobanoglous, G., *et al.* [106]

In the first mechanism, the hydroxyl radical attacks the organic compound, forming a H_2O and an organic radical. Then, there is the formation of the peroxide radical (RO_2•), an intermediate, which results from the attack by the O_2 molecule. Finally, the peroxide intermediate undergoes sequential reactions until the formation of CO_2 and H_2O (best scenario).

The electron transfer mechanism is the main mechanism in the degradation of organic halides. Due to the presence of this more electronegative element, there is the formation of an organic radical cation and a hydroxyl ion[121].

In the case of unsaturated or aromatic compounds, such as PAHs, the main mechanism is electrophilic addition. In the mechanism, the hydroxyl radical is added to the carbon, breaking the double bond. With this, there is the formation of a radical alcohol/phenol, which will follow in radical reactions[122].

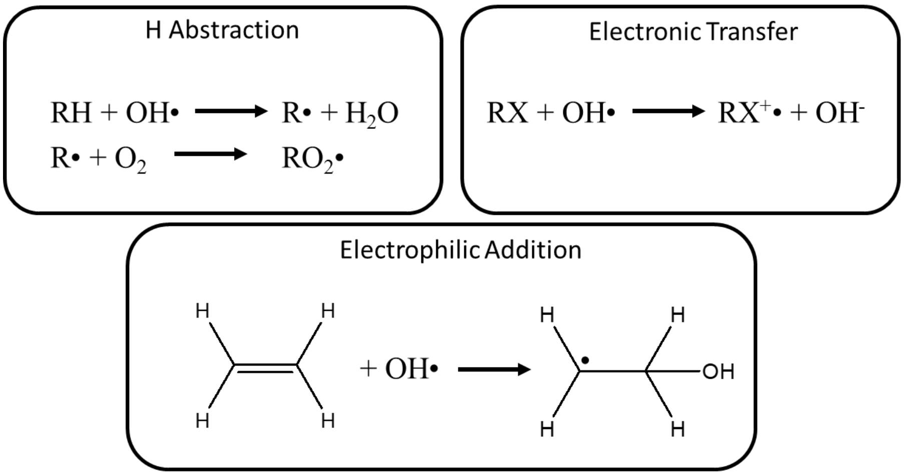


Figure 13. Degradation mechanisms by AOPs.

The AOPs can be divided into two classes: homogeneous and heterogeneous. Subsequently, each process can be subdivided into techniques that apply energy or not, as illustrated in Figure 14. Photolysis with or without addition of an oxidizing agent could be a promising technique to decontaminate PAHs firefighter's turnout, considering that they are simple and inexpensive methods that do not require the use of large amounts of water or specific facilities. Several AOP methods are described and used with the objective of degrading PAHs in water or soil[112,113,117–119,123]. Although there is no report of its application for decontamination of firefighter PPE.

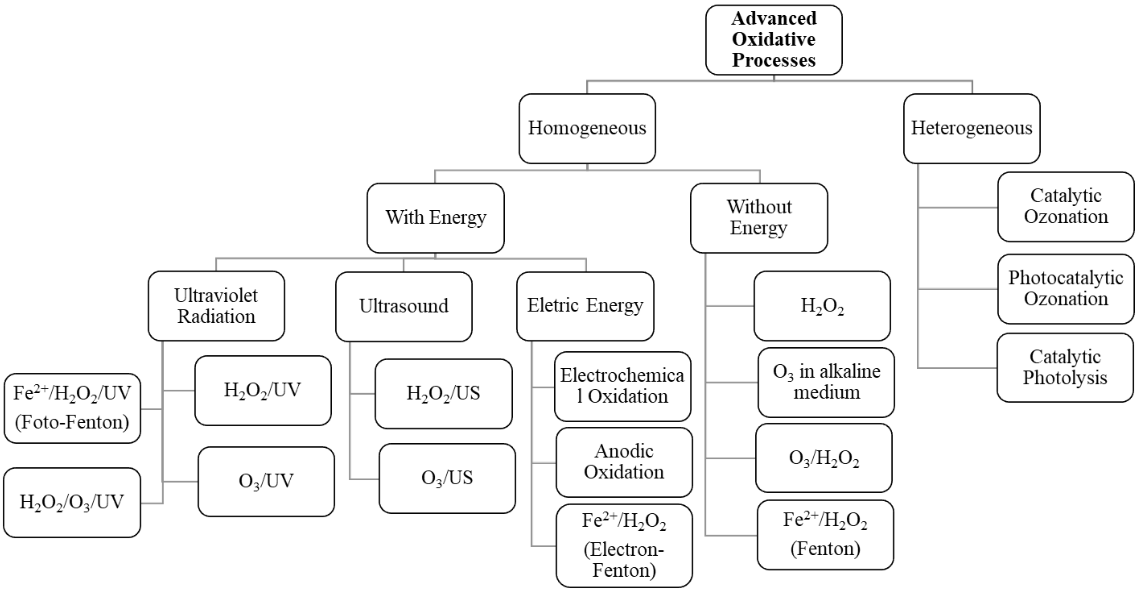


Figure 14. Classification of Advanced Oxidative Processes. Adapted from Poyatos *et al.*[100].

Photolysis is the use of a light source (ex.: sunlight or UV) to start radical reactions. For instance, PAHs molecules are excited (eq. 9) and transformed in a radical cation and a free electron (eq. 10). Then, e^-, when reacting with oxygen, forms the radical oxygen species ($O_2•$) and singlet oxygen ($^1O_2$), (eq. 11 and 12). Finally, the oxygen species formed also react with PAHs, producing unstable intermediates (eq. 13 and 14), which would undergo oxidizing reactions up to mineralized (CO_2, H_2O, eq. 15[124]) or up to stable species be formed.

$$\text{PAH} + h\nu \longrightarrow \text{PAH}^* \tag{9}$$

$$\text{PAH}^* \longrightarrow \text{PAH}•^+ + e^- \tag{10}$$

$$e^- + O_2 \longrightarrow O_2•^- \tag{11}$$

$$e^- + O_2 \longrightarrow {}^1O_2 \tag{12}$$

$$\text{PAH/PAH}•^+ + O_2•^- \longrightarrow \text{Intermediaries} \tag{13}$$

$$\text{PAH/PAH}•^+ + {}^1O_2 \longrightarrow \text{Intermediaries} \tag{14}$$

$$\text{Intermediaries} \longrightarrow CO_2 + H_2O + \text{inorganic ions} \tag{15}$$

Photolysis of PAHs is favored because these compounds frequently absorb in UV range (210-386 nm)[111,124]. Jacobs *et al.*[125] performed direct photolysis mediated by sunlight of pyrene, phenanthrene and naphthalene present in effluents contaminated with creosote, a toxic hydrocarbon solvent. They identified that the degradation rates decreased with decreasing of molecular weight. For instance, degradation rate of naphthalene is approximately two orders of magnitude slower than that of pyrene, since larger compounds are more reactive due to their higher extinction coefficients.

The effect of UV light (λ=254 nm) on the photolysis of anthracene, benzo(a)pyrene and fluoranthene compounds was studied by Sanches *et al.*[111]. Anthracene and benzo(a)pyrene showed degradation rates of 83-93% in groundwater and 36-48% in surface waters. The difference in rates in different media is because in surface waters there is more organic matter, which prevents the penetration of light, in addition to generating by-products that promote terminal radical reactions. For fluoranthene, rates of 13-54% were obtained in both matrices.

In soil, degradation of pyrene was also carried out under ultraviolet light. Zhang *et al.*[116] showed a maximum reduction of 35% in pyrene concentration at 30ºC after 32 days irradiation. Because in solid diffusion and OH• radicals' formation are not favored, long reaction time was required. Even after a long exposition, only moderate degradation was achieved.

1.3.Hydrogen peroxide

Oxidizing agents also promotes the degradation of PAHs. Hydrogen peroxide is one of the most used oxidizing agents and the formation of the OH• radical occurs as described in equation 16[103]. Subsequently, the OH• radical attacks the double bonds of the pollutants promoting the mineralization of the compounds (eq. 17). Equation 16 can be favored with the use of ultraviolet radiation, breaking the O-O bond of H_2O_2[99].

$$H_2O_2 \longrightarrow 2OH\bullet \qquad (16)$$

$$PAH + OH\bullet \longrightarrow \text{Intermediaries} \longrightarrow CO_2 + H_2O \qquad (17)$$

Shemer and Linden, studied the degradation of fluorene, dibenzofuran and dibenzothiophene in aqueous solution in the presence of hydrogen peroxide and UV radiation was evaluated. After evaluating the optimal conditions, the addition of hydrogen peroxide led to a significant increase in the removal rates and efficiency of all three PAHs studied.

The addition of hydrogen peroxide also favors the degradation reaction of PAHs in solid matrices. Gizem Eker and Sengul[119] analyzed the degradation of 12 PAHs present in soil samples from industrial areas. With the addition of 1% of H_2O_2, the group obtained a reduction of 88%, similar to the rate obtained with the use of a photocatalyst (TiO_2). Without the use of an oxidizing agent, it was possible to only degrade 35% of the total contaminants.

Regarding the decontamination of fabrics contaminated with PAHs, it should be noted that there is no record in the literature of the use of advanced oxidative processes, specifically photolysis and the use of an oxidizing agent. Considering the positive results in solution and solid samples, this work will evaluate the application of these AOPs in the decontamination of fabrics contaminated with PAHs. In addition to the removal, the integrity of the fibers will be evaluated, so that the decon processes does not change the properties of the PFPC.

2. Objectives

In this chapter, the general objective to investigate the effectiveness of some methods in the decontamination of Proximity Firefighting Protective Clothing. The aim is to maximize the removal of polycyclic aromatic hydrocarbon pollutants while minimizing damage to the fabric fibers, in order to maintain the integrity and thermal and physical properties of the PFPC.

The specific objectives of the work consist of:

- Apply photolysis with white lamp (WLP) and UV lamp (ULP) in the degradation of PAHs 9-methylanthracene and pyrene deposited on the fabric of the firefighter's suit;
- Determine the optimal reaction conditions (time, % H_2O_2 and irradiation source) for decontamination of contaminated turnouts by photolysis ;
- Evaluate the fibers of the outer shell fabric after treatment with a binocular biological microscope with an ocular lens, scanning electron microscope Energy Dispersive X-ray Spectroscopy, attenuated total reflection Fourier transform infrared spectroscopy technique tearing strength;
- Finally, compare the optimized decontamination route with the most used physical decontamination routes (wet-soap brushing and laundering).

3. Materials and Methods

3.1.Reagents

The analytes 9-methylanthracene (9MA, 98%) and pyrene (PYR, 98%) were purchased from Sigma-Aldrich and used without additional purification. Acetonitrile, suitable for HPLC with purity greater than 99.9%, was purchased from the companies Exodo and JT Baker. Synth brand hydrogen peroxide (H_2O_2) was used in the experiments with a concentration of 35% w/v. The water used was deionized (≥10 MΩ cm-1), produced in a Milli-Q purification system.

3.2.Equipment

- Photo-reactor;
- Mixed black lamp bulb, Empalux®, 250 W, 220 V;
- Mixed white lamp, Sollar® Lamp 250 W, 220V:
- Analytical balance 250g, BEL Equipment, model M254Ai, precision of 0.0001 g;
- Ultrasound bath with heating, Solidsteel, model 1400, 10 L;
- Micropipette, Labtex, model MC902554, 200 - 1000 μL;
- Micropipette, BioPet, model CU0083320, 0.5 - 10 μL;
- Micropipette, Pegapet, model 000063531; 100-1000 μL;
- Micropipette, Pegapet, model 000062706; 10-100 μL;
- Glass rod;
- Test tubes without rim, 18x180 mm, 35 mL capacity;
- Amber vials with septum and cap, maximum capacity 2 mL;
- Amber feather bottle with screw cap and 30 mL stopper;
- 25 mL Volumetric Flask;
- 10 mL Volumetric Flask;
- Binocular Biological Microscope with ocular lens, Biofocus
- Brasdonto sterilization oven, Model 3.
- Fluorolog Spectrofluorimeter, Horiba Scientific.
- Quartz cuvette, volume: 3.5 mL, Ioncell;
- Ultraviolet/Visible Spectrophotometer (UV/VIS), Varian, model Cary 5000;
- Fourier Transform Infrared Spectrometer (FTIR) with Attenuated Total Reflection (ATR) accessory, Term IS-10;

- Scanning Electron Microscope (SEM), Zeiss, model EVO 15;
- Energy Dispersive Spectrometry (EDS) Oxford UltimMax 40;
- Mass Spectrometer, Agilent, model 5973 inert;
- Gas Chromatograph, Agilent, model 6890N;
- Rxi®-1ms capillary column, with 100% methylpolysiloxane measuring 25 m X 0.20 mm X 0.33 µm, RESTEK;
- Nuclear Magnetic Resonance, Bruker Avance III HD 600 MHz equipped with 5 mm Broadband Observe (BBFO) probe.

3.3.Glassware cleaning

All glassware was washed with a neutral soap solution and rinsed with deionized water. Subsequently, rinses were carried out with the solvents ethanol (Synth), ethyl acetate (Synth) and dichloromethane (Merk), all of them were HPLC grade.

3.4. Stock Solution

To perform the tests, a 0.005 mol.L^{-1} solution was prepared containing pyrene and 9-methylanthracene (0.0025 mol.L^{-1} each). To prepare this solution, 2.5 mmol of the 9-methylanthracene compound were dissolved in 50 mL of acetonitrile in a volumetric flask. The same procedure was reproduced for pyrene and then the two solutions were unified to form the stock solution with a total concentration of 0.005 mol.L^{-1} in 100 mL.

3.5.Analytes characterization

Solutions of pyrene and 9-methylanthracene in acetonitrile (0.0025 mol.L^{-1}) each were characterized by UV/VIS spectrophotometry, and the absorption spectra of the analytes individually and of the stock solution (described in 3.5) were obtained. In addition, the analysis of the pure compounds and the mixture was carried out in a Gas Chromatograph coupled with a Mass Spectrometer (GC/MS) to obtain their retention times and fragmentation patterns, respectively.

Finally, the analysis by Nuclear Magnetic Resonance Spectroscopy (H-NMR) of the one-dimensional Hydrogen-Deuterium atom was also performed. The spectra were obtained using a Bruker Avance III HD 600 MHz Nuclear Magnetic Resonance spectrometer equipped with a 5 mm Broadband Observe (BBFO) probe, located at the NMR Laboratory at the Chemistry Institute of the University of Brasília. Reagents were solubilized in deuterated chloroform and tetramethylsilane (TMS) was added for referencing. Data processing was performed with TopSpin 4.1.3 software.

3.6.Discoloration test

Considering that hydrogen peroxide has a bleaching effect, to determine the concentrations used, a test was carried out to verify this effect on the fabric. For this, 1mL of a H_2O_2 solution was added to a 3x3 cm^2 piece of fabric. After the addition, the fabric rested for 24 hours and was observed at an optical microscope. The concentrations described in Table 7 were evaluated, and the dilutions were made with deionized water.

Table 7. Concentration of solutions used in the discoloration test.

	[Pure]	**[D1]**	**[D2]**	**[D3]**	**[D4]**	**[D5]**	**[D6]**	**[D7]**	**[D8]**	**[D9]**
[H_2O_2] %	35	3,5	0,35	0,035	0,0035	0,00035	0,000035	3,5E-06	3,5E-07	3,5E-08
[H_2O_2] mol.L^{-1}	10,289	1,0289	0,10289	0,010289	0,001029	0,000103	1,03E-05	1,03E-06	1,03E-07	1,03E-08

3.7. Experimental Design

The main objective of this chapter was to determine/apply a decontamination method to remove polycyclic aromatic hydrocarbon from Proximity Firefighting Protective Clothing. To do that, a five-step experimental design was performed (Figure 15). The first step was to determine the best conditions to perform the photolysis and promote the PAH removal in the outer layer of the firefighters' turnout. Three were tested: irradiation type (UV lamp, white lamp and without any lamp), percentage of H_2O_2 (0%, 0.35% and 3.5%) and reaction time (0, 1 and 3 days). Both the removal percentage and the fabric were analyzed. Considering all that, the best photolysis condition was determined and used in the next three steps. The second step of the experimental design was to identify the by-products formed after the PAHs photolysis in the outer layer fabric. The third step was to determine the kinetics of the photolysis reaction performed on the outer layer turnout fabric. For the fourth step, further analysis was made of the outer layer fabric after a long exposure (30 days) to the white lamp. Finally, the fifth step was to compare the best photolysis condition with the traditional techniques (wet-soap brushing and laundering). At this stage, the tests were performed on the three-layers fabric, to reproduce a more realistic scenario. The experimental conditions and other details will be discussed in the next topics of this thesis.

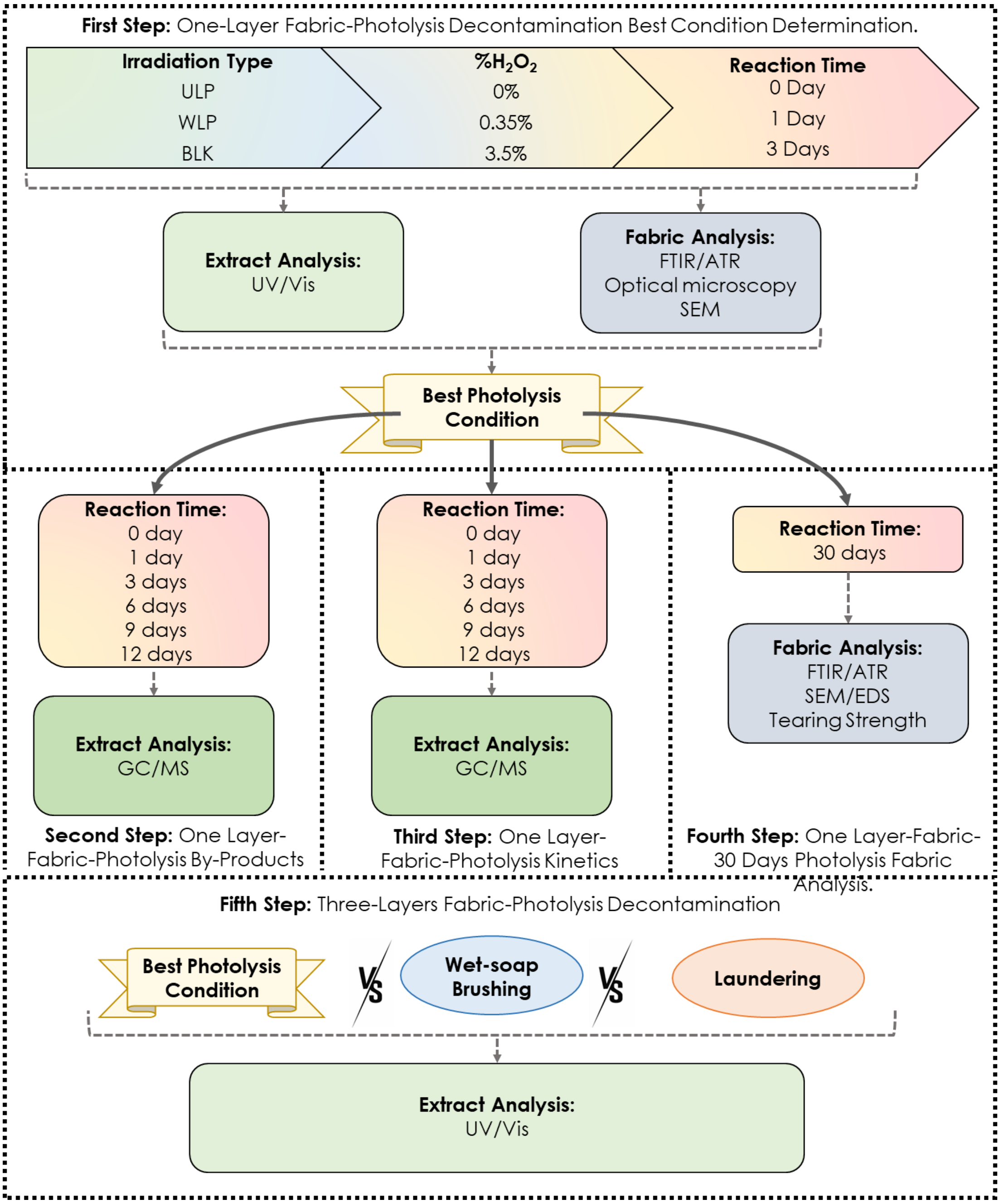


Figure 15. The experimental design divided into five steps.

3.8. First Step: One-Layer Fabric-Photolysis Decontamination-Best Condition Determination.

To determine the best photolysis condition, pieces of fabric from the outer layer of the firefighters' turnout were cut into squares measuring 3x3 cm^2 (Figure 16). The fabric used was new, from Unishell®, donated by Santanense Workwear, and present a nominal composition of 58% para-aramid (kevlar®), 40% meta-aramid (nomex®) and 2% carbon.

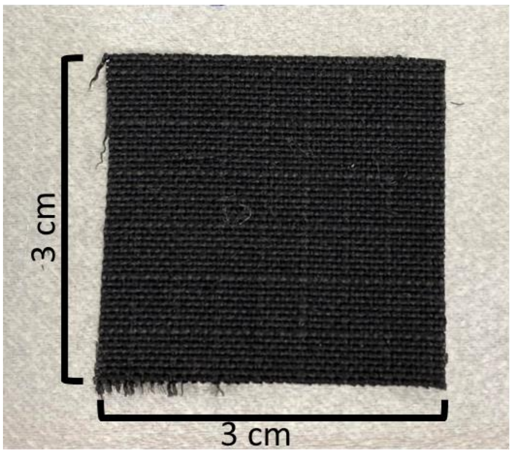


Figure 16. Unishell® fabric sample used in the experiments.

The photolysis was carried out inside the photoreactor (Figure 17) varying three conditions: type of irradiation, % of H_2O_2 and reaction time. The photoreactor was built using a wooden box with a reflective surface inside. The structure is equipped with a lamp inlet and two coolers to promote cooling and airflow. The experiments were carried out with an UV lamp (ULP), a white lamp (WLP) and without the light irradiation (BLK). The lamps used in the experiment were: mixed white 250 W, model E27, Luz Sollar® and mixed ultraviolet (a black lamp) of 250W, Empalux®. The H_2O_2 concentrations used were 0%, 0,35% and 3,5% of H_2O_2. Finally, the photolysis was done during 0, 1 and 3 days and was established considering the work regime of the CBMDF firefighters, which is 24 hours of service and 72 hours of rest. Also, an experiment was performed inside an oven in the dark, to evaluate the thermal effect in the PAH removal/volatilization. All experiments were done in triplicate.

Before the start of the test, 200 µL of the stock solution were added to the fabric samples and spread with the aid of a glass rod. Then, the solution was air-dried for 10 minutes at room temperature. **In three pieces of fabric no stock solution was added, in other to perform the fabric analysis**. After 10 minutes, 200 µL of H_2O_2 were added to the PAH contained fabric samples.

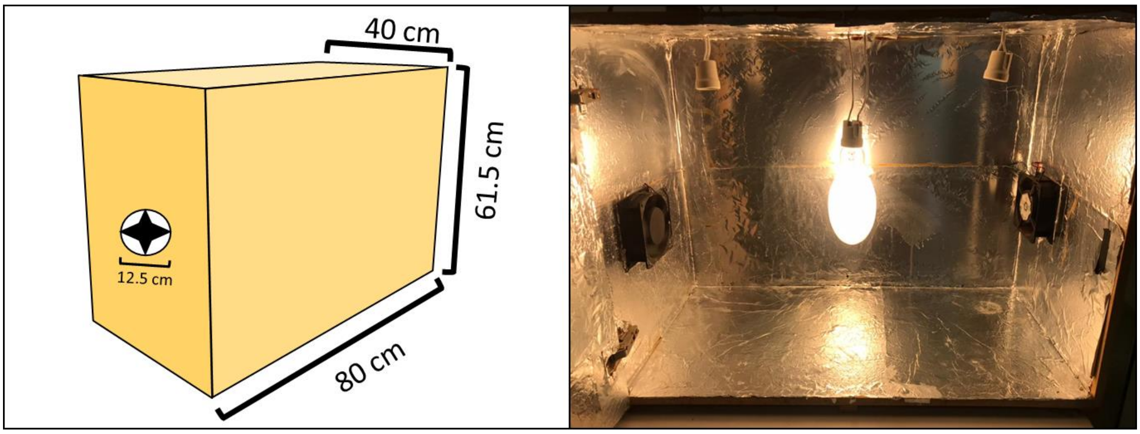


Figure 17. Photo-reactor used in carrying out the experiments equipped with white lamp.

3.8.1. Extract Analysis by UV/VIS

After the photolysis took place, the fabric samples were extracted in a test tub with 10 mL of acetonitrile. Each tube was placed into an ultrasonic bath for 20 min at room temperature. After extraction, the extracts were stored in amber flasks in a freezer and latter analyzed by UV/VIS spectroscopy.

The absorption spectra of extracts (Varian ultraviolet/visible spectrophotometer, model Cary 5000) were obtained to determine the concentration of each target compound. For this, a dilution of the extract/acetonitrile volume of 1:1 (outer shell fabric experiments) and 1:2 (three-layer fabrics experiments) was made, so the maximum absorbance obtained were close to 1. The spectra were obtained in the 220-400 nm range. The spectra areas were obtained using the Origin® software.

Quantification was obtained by analytical curves of. spectrum of samples without the PAH were also obtained and absorbance values were subtracted from those values measured for the samples for the concentration determination.

3.8.1.1. UV/VIS Calibration

The analytical curve was obtained using the least squares regression, using the linear regression model, analysis of variance (ANOVA) and F test were applied to determine regression significance.

For the elaboration of the curve, six standard solutions were prepared by diluting the stock solution (item 3.5) containing the pyrene and 9-methylanthracene analytes, with the concentrations described in Table 8. For each standard, three readings were performed.

Table 8. Concentration of standard solutions.

Solution	Concentration (mmol.L^{-1})
Stock Solution	5,15
Standard Solutions 1	0,0515
Standard Solutions 2	0,0429
Standard Solutions 3	0,0271
Standard Solutions 4	0,0206
Standard Solutions 5	0,0158
Standard Solutions 6	0,0103

3.8.2. Fabric Analysis

To assess whether the photolysis decontamination promoted the deterioration of the outer shell fabrics used in firefighting protective clothing, Unishell® samples were analyzed. All analysis were performed using samples that were treated (**without the PAH**) according to the conditions described in item 3.7. for 3 days reaction.

3.8.3. Fourier Transform Infrared Spectroscopy with Attenuated Total Reflectance (ATR/FTIR).

Infrared analysis was carried out using a Thermo Scientific Nicolet iS10 FTIR Spectrometer with The Thermo Scientific Smart iTX ATR sampling accessory, from INC/PF Laboratory. Spectra were collected in the range of 4000 – 460 cm^{-1}, with a DTGS detector, KBr beamsplitter, and a HeNe laser.

For each fabric sample, 10 FTIR spectra were collected at different places and the means were obtained. Spectral baseline correction, analysis and normalization was carried out using Origin 2021 software.

3.8.4. Binocular Microscope

Images of fabric fibers using a binocular microscope equipped with digital eyepiece lens were obtained before and after the treatment (samples treated without the PAH). The equipment was available at the Chemistry Laboratory in Federal Institute of Brasília, campus Samambaia.

3.8.5. Scanning electron microscopy with energy dispersive X-ray spectrometry SEM/EDS

SEM/EDS images were obtained of fabric fibers after the treatment using a Zeiss, model EVO 15, Scanning Electron Microscope with EDS Oxford UltimMax 40 from INC/PF Laboratory. Fiber diameters were obtained using the Gwyddion® 2.60 software, measuring 10 points in 5 images (2 points/image) for each sample. The images were obtained using backscattered electrons detector and low vacuum, without conductive coating on the sample. For the compositional maps, a 40mm square silicon detector was used and the software AzTech.

3.9. Second Step: One Layer-Fabric-Photolysis-By-Products

After the best photolysis condition was determined, considering both the % of PAHs removal and fiber degradation, the extract obtained in the first step (item X) were analyzed with gas chromatograph coupled with mass spectrometer (GC/MS) in order to determine the possible by-products formed after the photolysis reaction.

3.9.1. Extract Analysis by GC/MS

The extract obtained after the 3-days photolysis reaction with WLP and 0% H_2O_2 (**same obtained in First Step and analyzed with UV/VIS**) were also evaluated by gas chromatograph coupled with mass spectrometer (GC/MS). The presence (qualitative analysis) and concentration (quantitative analysis) of the PAHs studied were evaluated by an Agilent model 6890N gas chromatograph coupled with an Agilent model 5973 inert mass spectrometer. The ASTM method 8270E[85] was used, with a Rxi®-1ms stationary phase capillary column, with 100% methylpolysiloxane of dimensions 25 m x 0.20 mm x 0.33 µm (RESTEK).

The injector temperature was maintained at 280°C, in Splitless mode with 1,3 µL injection. The column was maintained at a constant flow of helium at 0.5 mL/min. The chromatographic oven programming was: initial temperature of 40°C, held for 4 min, then heating at a rate of 10°C/min to 320 °C, keeping at this temperature for 2 min. The total time of analysis was 34 minutes. Solvent delay was used of 4,00 min and a gain factor of 20. The GC/MS interface was maintained at 280°C, and the mass spectrometer was operated in scan mode in the scan range from 35 to 500 m/z, with HiSense.u. The mass spectra obtained were analyzed using the Chemstation Data Analysis software and the NIST Search software (version 2.3). Quantification was conducted with external calibration curves with kwon concentrations of solutions containing 9-methylanthracene and pyrene.

3.9.1.1. GC/MS Calibration

To determine the concentration in the extracts obtained after the photolysis experiments, an external calibration was performed, using the method of least squares and the linear regression models was applied. Analysis of variance (ANOVA) and F test were applied to determine regression significance. The areas of each peak, referring to each analyte, were related to the concentrations of the six standard solutions used, described in Table 9. The retention time of each analyte was determined by the injection of pure analytes and by the analysis of the mass spectrum.

Table 9. Concentration (mmol.L^{-1}) of each analyte in the standard solutions.

	Concentration (mmol.L^{-1})	
	Pyrene	*9-Methylanthracene*
Standard Solutions 1	0.1035	0.1007
Standard Solutions 2	0.0828	0.0806
Standard Solutions 3	0.0621	0.0604
Standard Solutions 4	0.0414	0.0403
Standard Solutions 5	0.0207	0.0201
Standard Solutions 6	0.0052	0.0050

3.10. Third Step: One Layer-Fabric-Photolysis-Kinetics

Kinetics of the optimized photolysis reaction (type of irradiation and % of H_2O_2) was determinate in the reaction times: 0, 1, 3, 6, 9, 12 and 15 days. The experiment was performed as described in topic 3.9., whereas the extracts were obtained as previously described and stored in freezer for further analysis. Theses samples were analyzed with a gas chromatograph coupled to mass spectrometer, to determine the PAH concentration and to detect possible photolysis by-products.

3.11. Fourth Step: One Layer-Fabric-30 Days Photolysis Fabric Analysis.

Also, long exposure experiment (30 days) was performed with the best photolysis condition (type of irradiation and % of H_2O_2 – WLP and 0% H_2O_2) using the outer layer fabric. After the irradiation with the lamp, the fabric was analyzed with ATR/FTIR and

SEM/EDS, as described previously. Also, a tear resistance test was performed in the fabric before the irradiating and after.

3.11.1. Tearing Strength.

The tear resistance test was performed in accordance with ASTM D2261:2013 (2017)e1[126], Standard Test Method for Tearing Strength of Fabrics by the Tongue (Single Rip) Procedure (Constant-Rate-of-Extension Tensile Testing Machine). The experiment conditions are described in Table below.

Table 10. Tearing Strength experiment conditions.

Distance between the claws	75 mm
Speed	50 mm/min
Dynamometer Type	CRT
Calculation Methodology	Average of 5 peaks
Software Used	Bluehill 3
Dimensions of the Claw	Front: 2.5 mm x 7.5 mm Back: 2.5 mm x 7.5 mm
Tear Direction	Parallel to the warp and to the weft

For this analysis, only the best photolysis condition (type of irradiation and % of H_2O_2 – WLP and 0% H_2O_2), described in experiments from item 3.8. was used. Only this sample was analyzed because the experiment was difficult to access and was expensive. The outer shell (without PAH) sample was treated for 30 days, so that a long exposure evaluation could be done.

3.12. <u>Fifth Step:</u> Three-Layers Fabric-Photolysis Decontamination

In order to analyze the effect of the white lamp-photolysis decontamination on a more realistic scenario, the decontamination was carried out in samples of three-layers fabric from Brazilian proximity firefighters' protective clothing. The fabrics from the jackets and suits turnout were cut into 10 cm diameter discs and sewn together in the same order that is used by Brazilian firefighters (Figure 18). The fabrics were obtained from a costume donated by CBMDF. As it was a used costume, the fabrics were washed beforehand to remove any contaminants. The outer layer was composed: 36% Viscose FR; 56% Meta Aramid; 6% Para-Aramid; 2% Antistatic fiber (± 7% tolerance for each component).

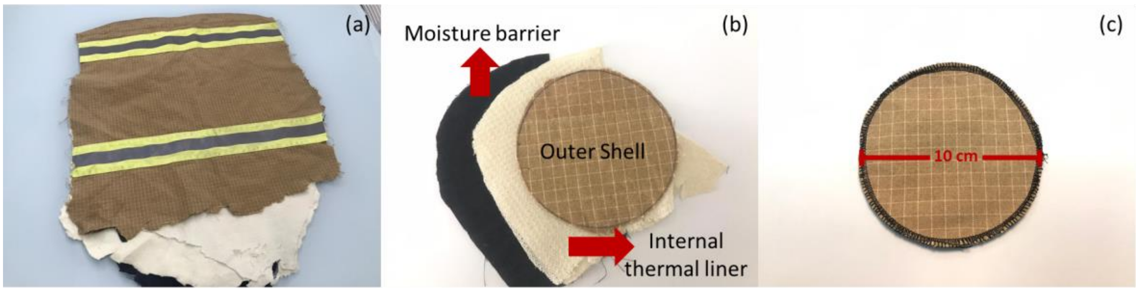


Figure 18. Samples of the real fabric used in the photolysis experiments, being **(a)** sample of the donated approximation cap, **(b)** the three layers of the PFPC and **(c)** discs with the three layers sewn together.

For the photolysis experiment, each disc was contaminated with 1.8 mL of the PAH stock solution and air-dried for 10 minutes. The best reaction conditions found in the previous tests (type of irradiation, reaction time and quantity of H_2O_2 added) were reproduced. As the outer shell fabric no longer had the repellant coating, it was not necessary to spread the solution with the glass rod. For the extraction procedure, 80 mL of acetonitrile with ultrasonic bath for 20 min at room temperature were done. The experiment was done in triplicate.

3.12.1. Physical Decontamination.

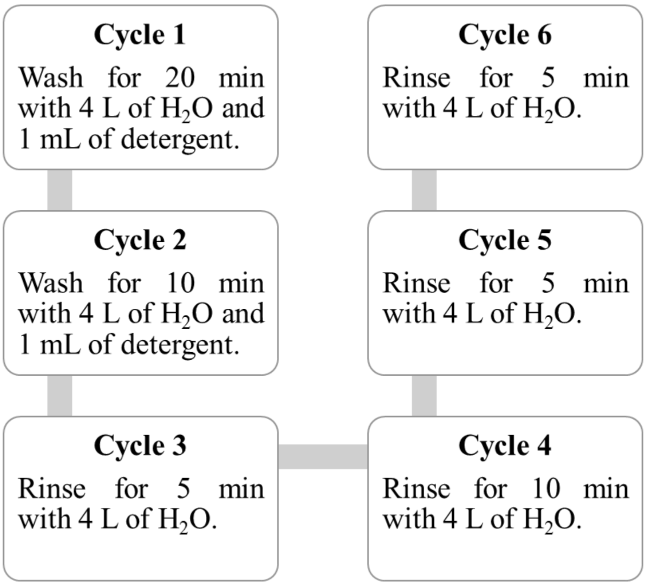
To compare the photolysis decontamination with physical well-established decontamination procedures, a series of experiments were carried out in three-layer fabrics samples. The physical decon techniques evaluated were wet-soap brushed or laundered.

For the wet-soap brushing, the procedure described by Fent *et al.*[64] was adapted. A neutral soap (0.5 mL of soap in 380 mL of water) solution was poured in a pre-soaked three-layer sample, using a spray bottle. Then, the disk was scrubbed 10 times with a plastic bristle brush and rinsed quickly, preventing water from penetrating the last layer of the turnout.

To evaluate the efficiency of laundering, an experiment using a bucket and a mechanical stirrer was carried out, emulating a washing machine (Figure 19). The emulated configuration was chosen (instead a real washing machine) to reduce dilution effect. The simulated laundering was adapted following the methodology described by NFPA 1851[75], describe in Figure 20. Two washing cycles were done with 1 mL of commercial liquid laundry detergent, first for 20 minutes and second for 10 minutes.

Then, three rinse cycles were done: one for 10 minutes and two more for 5 minutes each. In all cycles, 4 L of water were added and after its time, the water was completely drained.

Figure 19. Simulating a washing machine



Cycle 1
Wash for 20 min with 4 L of H_2O and 1 mL of detergent.

Cycle 2
Wash for 10 min with 4 L of H_2O and 1 mL of detergent.

Cycle 3
Rinse for 5 min with 4 L of H_2O.

Cycle 4
Rinse for 10 min with 4 L of H_2O.

Cycle 5
Rinse for 5 min with 4 L of H_2O.

Cycle 6
Rinse for 5 min with 4 L of H_2O.

Figure 20. Laundering cycles.

4. Results and Discussion

4.1.Characterization of analytes

Two PAH were chosen as target analyte to investigate photolysis effectiveness. Pyrene (PYR) was chosen because of its presence in post-fire samples, as described by Thomas *et al.*[21]. 9-Methylanthracene (9MA) was selected because in forest fires and in lower temperature fires, there is the formation of PAHs substituted with alkyl groups[55,56]. In addition, both compounds were used as a model in work carried out by Lucena *et al.*[98] and Mauricio[127], thus it would be easier to compare the results. The concentration used in the experiments conducted in these chapter were also adapted from Lucena *et al.*[98] To allow extraction, analysis by GC/MS and UV/VIS after the experiments, it was necessary to use higher PAH concentration when compared to Chapter 2 of this thesis.

The structures of the PAHs used in the present study were confirmed by one-dimensional ^{1}H-NMR. The ^{1}H-NMR spectrum of the 9-methylanthracene and the signal assignment are shown in Figure 21 and Table 11. Also, the ^{1}H-NMR of the deuterated solvent used was carried out.

The signals found at 9MA ^{1}H-NMR spectrum are in agreement with what is described in the literature[128]. The molecule has a plane of symmetry, so that there is chemical equivalence between the hydrogens. Signal **6** refers to the methyl group, showing chemical detachment in the range of CH_3-Ar (2.0 – 3.0 ppm[129]). The other signs show chemical detachment in the range of aromatic hydrogens (6.5 – 8.0 ppm). The singlet (sign **1**) refers to the aromatic hydrogen in the para position of the methyl group. Signal **2** corresponds to a double doublet, and it couples with an H ortho (J = 8.80 Hz), an H meta (J = 2.96 Hz) and an H para (J = 0.92 Hz). Signal **3**, a double triplet, comes from a coupling with one H ortho (J = 8.44 Hz) and two H meta (J = 0.73 Hz). Finally, signals **4** and **5** are two double doublets, corresponding to the coupling with two H ortho (J = 8.80, 8.27 and 8.24 Hz) and one H meta (J = 1.31, 1, 48, 1.07 and 1.29 Hz).

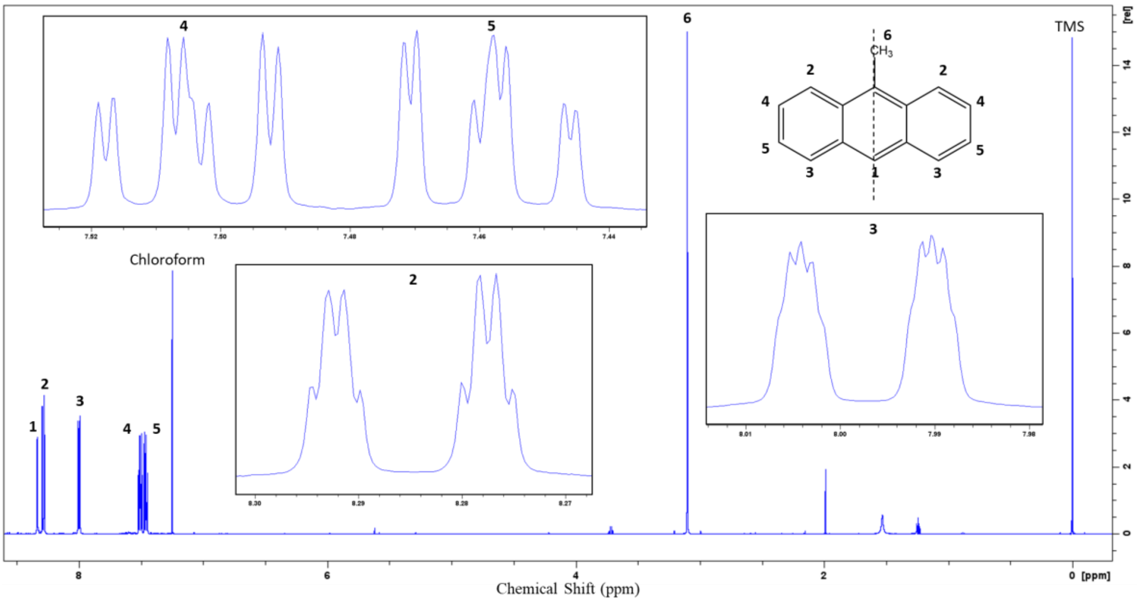


Figure 21. ^{1}H-NMR spectrum (600 MHz) of PAH 9-methylanthracene in $CDCl_3$ with TMS.

Table 11. Signal assignment of the ^{1}H-NMR spectrum (600 MHz) of PAH 9-methylanthracene in $CDCl_3$ with TMS.

Signal	Chemical Shift (ppm)	Multiplicity	Coupling Constants(J)	Integral
1	8.33	Singlet	-	1
2	8.29	Double doublet of doublets	8.80 and 2.93 Hz 8.80 and 0.92 Hz	2
3	8.00	Doublet of triplets	8.44 e 0.73 Hz	2
4	7.51	Double doublet of doublets	8.80 and 1.31 Hz 8.80 and 1.48 Hz	2
5	7.46	Double doublet of doublets	8.24 and 1.07 8.27 and 1.29	2
6	3.10	Singlet	-	3

The pyrene (Figure 22) presents a simpler 1H NMR spectrum, due to the existence of two planes of symmetry in the molecule. The assignment of signals and other information is described in Table 12.

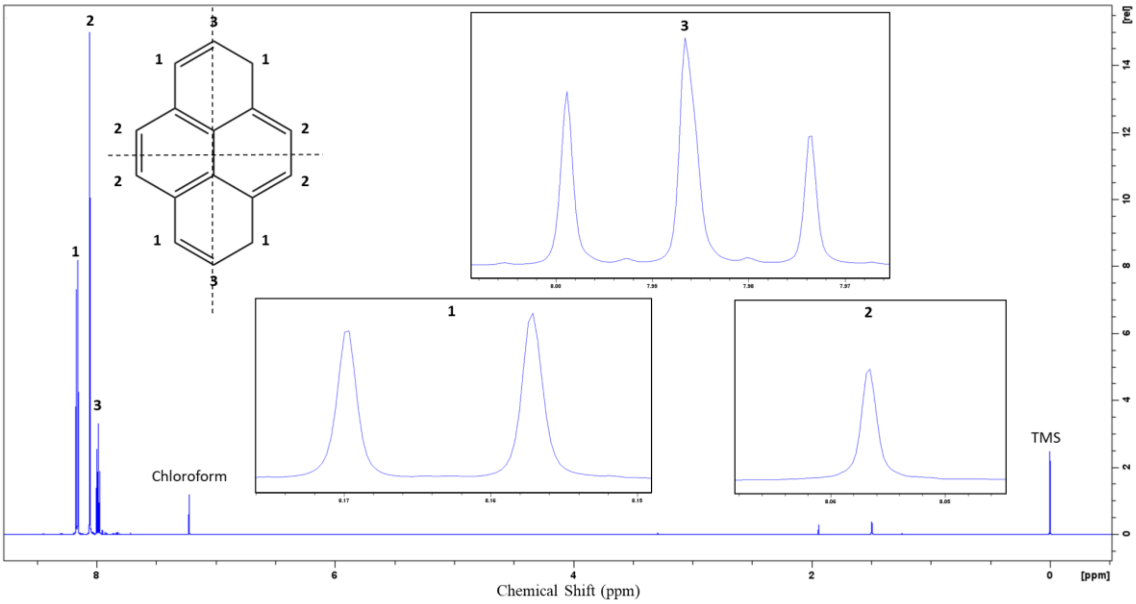


Figure 22. ^{1}H NMR spectrum (600 MHz) of pyrene PAH in $CDCl_3$ with TMS.

Table 12. Signal assignment of the ^{1}H-NMR spectrum (600 MHz) of pyrene in $CDCl_3$ with TMS.

Signal	Chemical Shift (ppm)	Multiplicity	Coupling Constants(J)	Integral
1	8.1697	Doublet	7.70 Hz	4
2	8.0566	Singlet	-	4
3	7.9864	Triplet	7.27 Hz	2

All signals show chemical shift in the range of aromatic hydrogens and are in agreement with the spectra found in the literature[130]. Signal **1**, a doublet, corresponds to coupling with an ortho hydrogen (J = 7.70 Hz). Singlet **2** refers to four -CH. Finally, the triplet in **3** refers to the coupling with two H ortho (J = 7.70 Hz).

The unsigned peaks in the ^{1}H-NMR spectra of Figures 21 and 22 come from contaminants in the solvents used (blank spectra were analyzed). In view of the signals and couplings obtained in the spectra above, the structure of the PAHs analyzed is in accordance with what was expected.

The compounds were also characterized by UV/VIS spectrophotometry, and the spectra of the acetonitrile solutions of the individual compounds and of the stock solution are described in Figures 23 and 24.

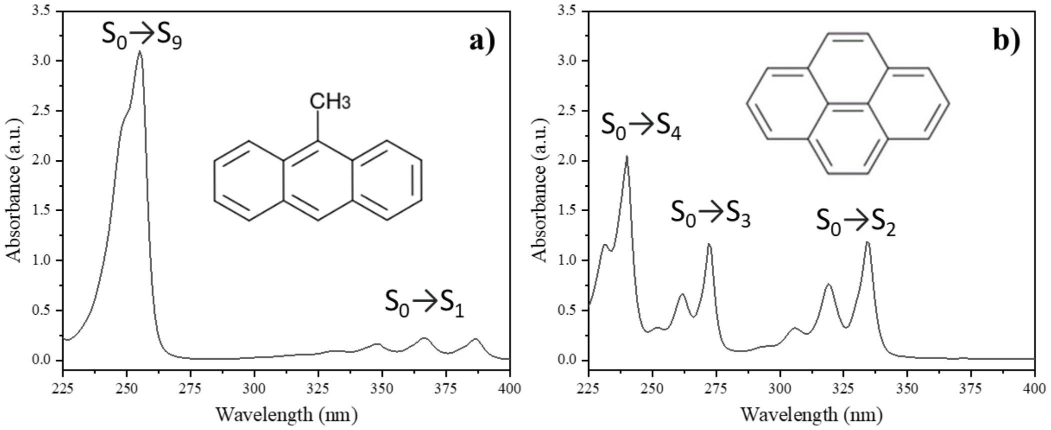


Figure 23. Absorption spectra of compounds: **(a)** 9-methylanthracene and **(b)** pyrene

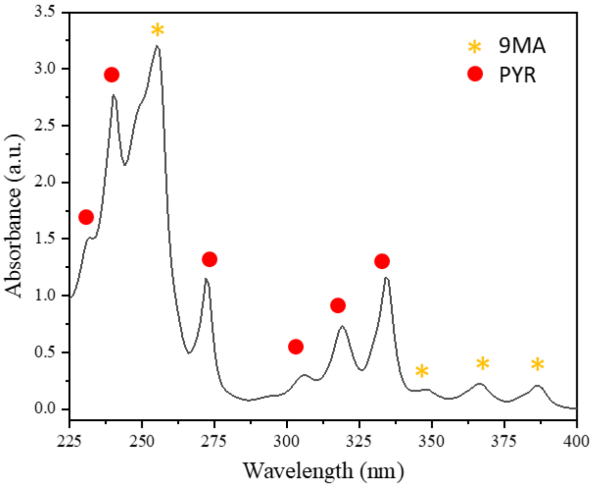


Figure 24. Absorption spectrum of the stock solution.

PAHs are known to absorb in the region 210 – 386 nm[113], a fact that can be confirmed by the spectra in Figure 23a and 23b. The characteristic bands of the compounds are also observed in the absorption spectrum of the stock solution (Figure 24) (marked with red spheres and yellow asterisks).

Individuals and the stock solutions were also characterized by the GC/MS technique. The chromatograms obtained are represented in Figure 25. The retention times obtained are described in Table 13. The mass spectra obtained by electron ionization corresponding to each compound in the chromatogram were obtained and are described in Figure 26. In the case of PAHs, due to their highly stable structure[131], it is possible to detect the molecular ion ($M^{+\bullet}$), which has high intensity. For 9-methylanthracene and pyrene, it is possible to visualize the molecular ions of mass-charge ratio 192 *m/z* and 202 *m/z*, respectively.

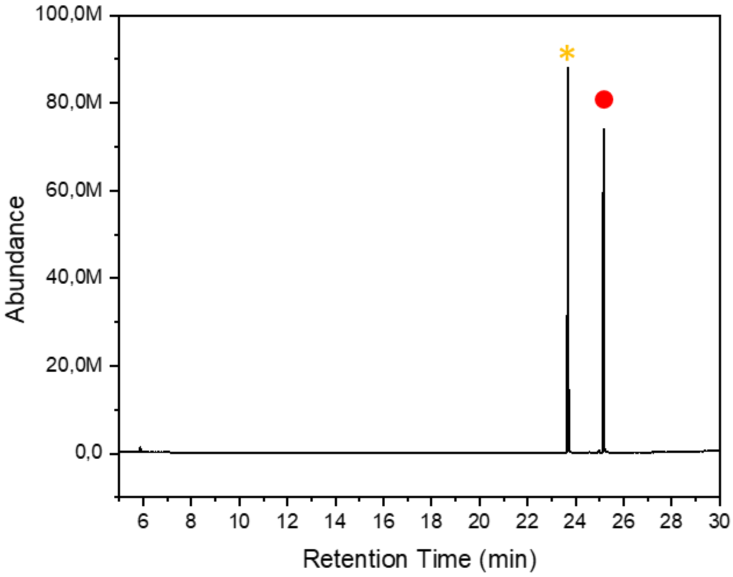


Figure 25. Chromatogram of the stock solution. Unlabeled peaks correspond to the chromatographic column.

Table 13. Retention times of analytes.

Analyte	Retention Time (min)
9-methylanthracene	23,673
Pyrene	25,166

It is also possible to detect doubly charged ions (M^{2+}) and their hydrogen adducts, a common fact in the mass spectrum of polycyclic aromatic hydrocarbons[131]. Furthermore, it is possible to identify ions referring to acetylene losses (26 m/z) from the tropylium ion and the phenyl ion. The structures and mass-charge ratios of the fragments identified in the mass spectra of 9-methylanthracene and pyrene compounds are described in Figure 27.

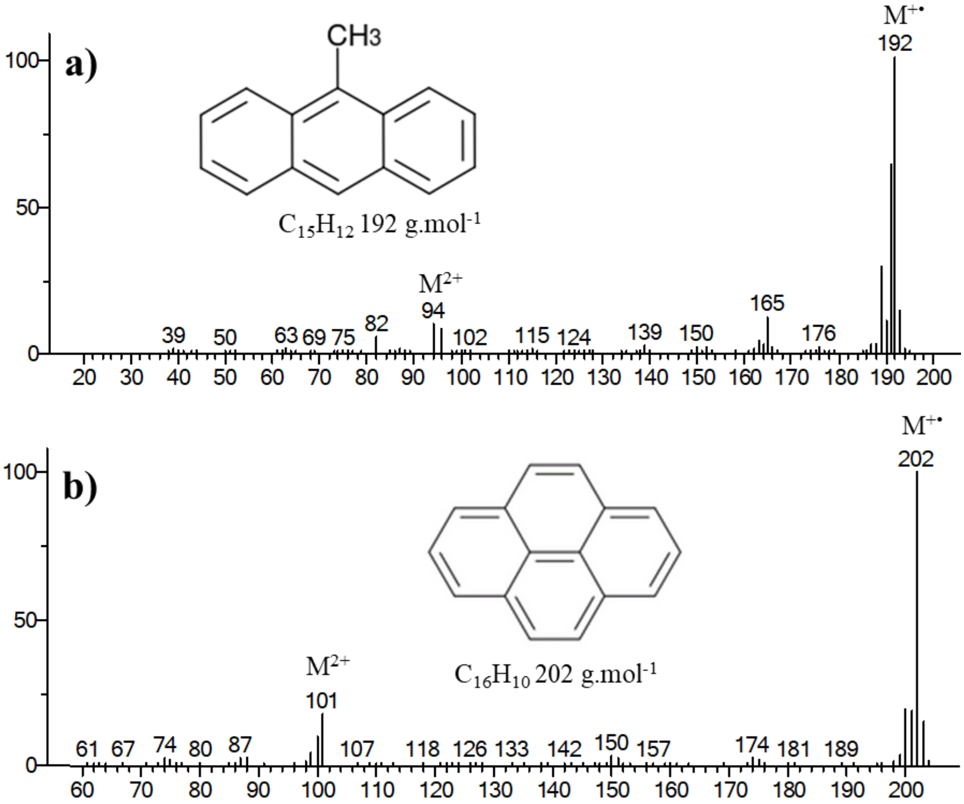


Figure 26. Mass spectra of compounds **(a)** 9-methylanthracene and **(b)** pyrene.

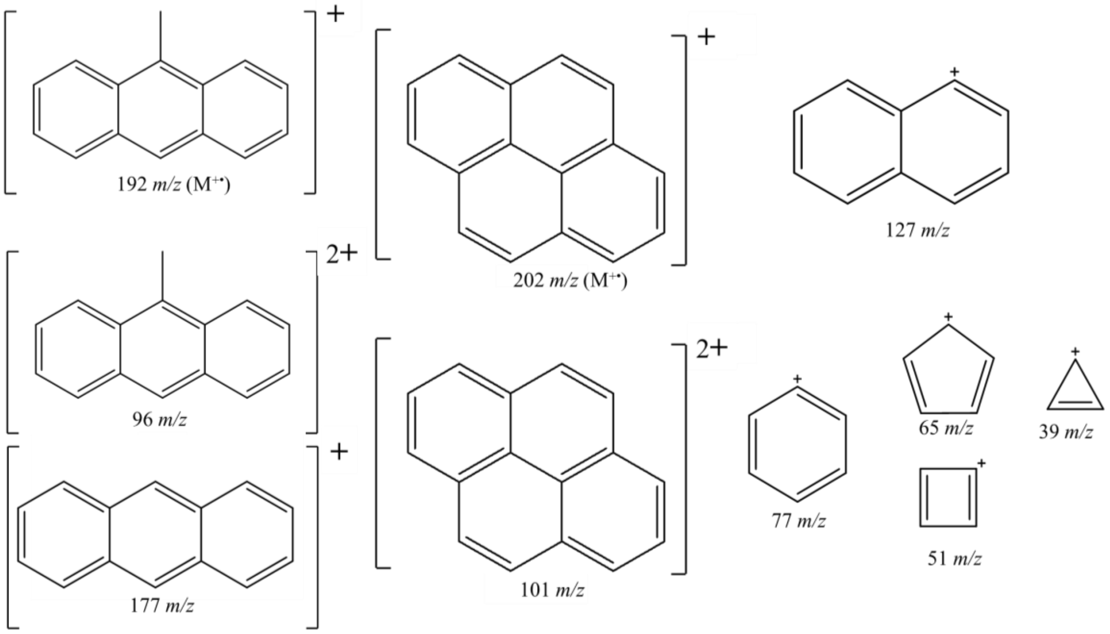
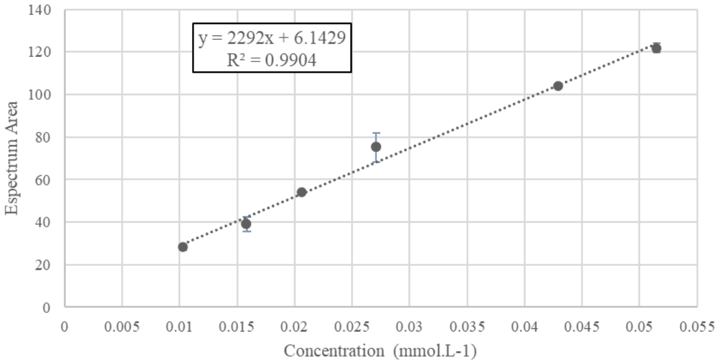


Figure 27. Main organic ion fragments obtained by electron ionization of 9-methylanthracene and pyrene analytes.

4.2.Calibration

4.2.1. UV/VIS

To determine the concentration of PAHs, an analytical curve was constructed in the range of 0.01 to 0.05 mmol.L^{-1} of the PAH mix. For that, the region of 220 – 400 nm of the standard solution was integrated. The coefficient of determination R^2 of the simple linear regression is described in Graph 25 and the ANOVA (Table 14) of the regression indicate that the linear fit is indicated.

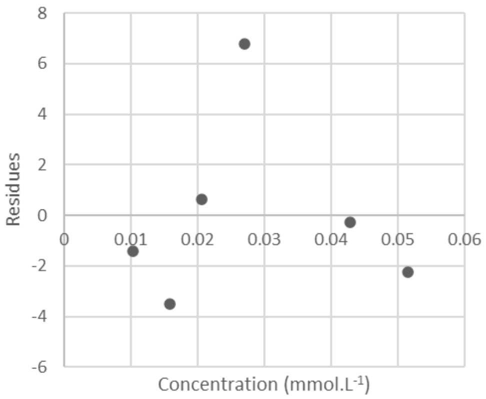


Graph 25. Analytical curve constructed using linear fit for UV/VIS analysis.

Table 14. UV/VIS ANOVA table for PAH solution.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	6780.34	1	6780.34
Residual	65.96	4	16.49
Lack of fit	65.96	4	16.49
Total	6846.30	5	1369.268

Linear regression homoscedasticity was also evaluated in the plot of residues versus concentration. Graph 26 demonstrates an uncorrelated and homoscedastic behavior, so that the errors are evenly distributed. Only one point that showed a greater deviation, so the Q test was applied to verify the existence of anomalous points. All points presented a value in the test above the critical value, being maintained in the regression.

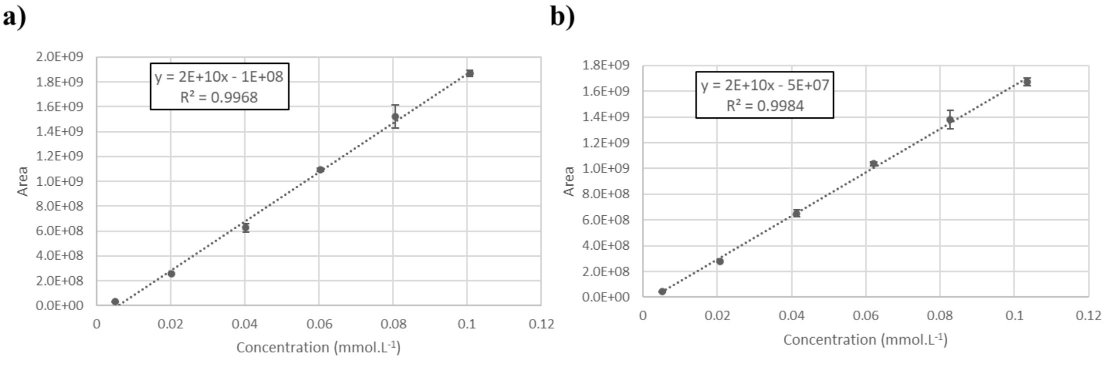


Graph 26. Analysis of residues versus concentration for UV/VIS analysis.

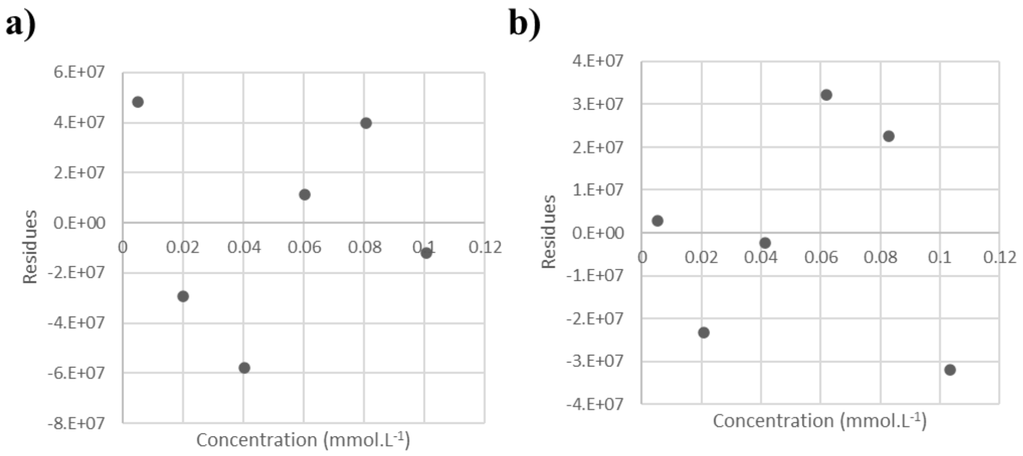
4.2.2. GC/MS

As done for the UV/VIS analysis, an analytical curve was constructed to determine the concentration in the extracts obtained in the experiments performed and analyzed by GC/MS. The curve was constructed with standard solutions of 9-methylanthracene and pyrene, separately, in the concentration range of 0.005 – 0.010 mmol.L^{-1}.

The curves for the compounds 9-methylanthracene (Graph 27a) and pyrene (Graph 27b) presented coefficients of determination equal to 0.9968 and 0.9984, respectively, consisting of acceptable values[86]. By analyzing the graphs of residuals versus concentration (Graph 28), it is possible to determine that the errors have a homoscedastic behavior.



Graph 27. Analytical curves constructed using linear fit for analytes **(a)** 9-methylanthracene and **(b)** pyrene for GC/MS analysis.



Graph 28. Residue analysis versus concentration curves for analytes **(a)** 9-methylanthracene and **(b)** pyrene for GC/MS analysis.

Tables 15 and 16 represent the analysis of variance of the analyte regressions. As the F test performed has a higher value than the one shown, it is possible to conclude that the regressions performed are adequate.

The limit of detection (LOD) and limit of quantification (LOQ) of the compounds 9-methylanthracene and pyrene were determined using the equation of the analytical curve, and the values obtained are described in Table 17.

Table 15. GC/MS linear fit regression ANOVA table for 9-methylanthracene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	2.65E+18	1	2.65E+18
Residual	1.36E+16	4	3.39E+15
Lack of fit	1.36E+16	4	3.39E+15
Total	2.67E+18	5	5.33E+17

Table 16. GC/MS linear fit regression ANOVA table for pyrene.

Source	***Sum of Squares***	***Degrees of Freedom***	***Mean Squares***
Regression	2.00E+18	1	2.00E+18
Residual	3.12E+15	4	7.81E+14
Lack of fit	3.12E+15	4	7.81E+14
Total	2.01E+18	5	4.02E+17

Table 17. Limits of detection (LOD) and quantification (LOQ), in mmol.L^{-1}, obtained by the analytical curves for the analytes

	9-methylanthracene	**Pyrene**
LOD	0.00021 mmol.l^{-1}	0.00016 mmol.l^{-1}
LOQ	0.00071 mmol.l^{-1}	0.00052 mmol.l^{-1}

4.3. Discoloration Test.

Before carrying out the photolysis experiments, the influence hydrogen peroxide in the fabric, which can change its color, acting as a bleach, was evaluated. The addition of an oxidizing agent could favor the photolysis of pollutants, being the most used the hydrogen peroxide[103]. The addition of H_2O_2 must be controlled and, at higher concentrations, termination reactions are favored. Two concentrations were used in this study.

In the discoloration test, H_2O_2 solutions were added to the fabric and let resting for 24h. After this period, **the solution did not completely evaporate, as seen in Figure 28 and 29**. When analyzing the photos (Figure 29) and images obtained with an optical microscope (Figure 30), it was not possible to identify any discoloration point of the fabric. Thus, the concentrations [D1] and [D2] were chosen to carry out the photolysis experiments with an oxidizing agent, considering the possibility to be high enough to promote the photolysis and low enough to not promote termination reactions. Once the hydrogen peroxide concentrations were chosen, the experiments were carried out with white lamp, UV and 0.35% and 3.5% and concentrations.

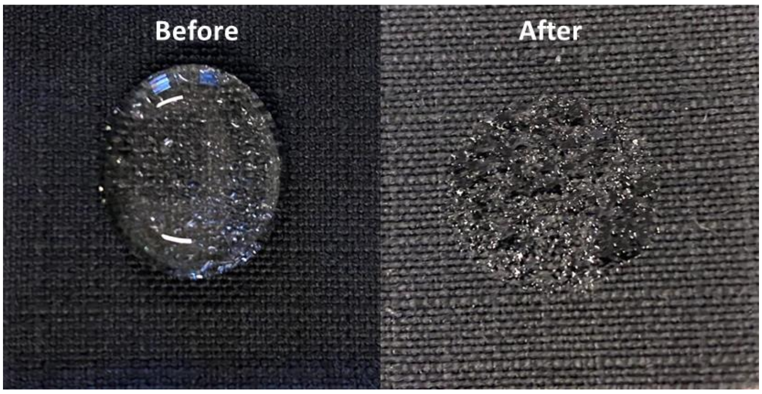


Figure 28. Photos of the discoloration test performed with the concentration 3,5x10^{-8} % [D9] before and after the 24-hour period.

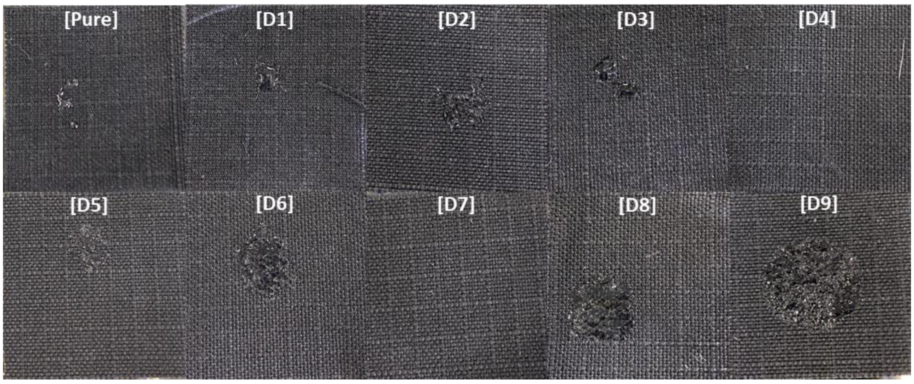


Figure 29. Photos of the discoloration test performed with the concentrations described in Table 7.

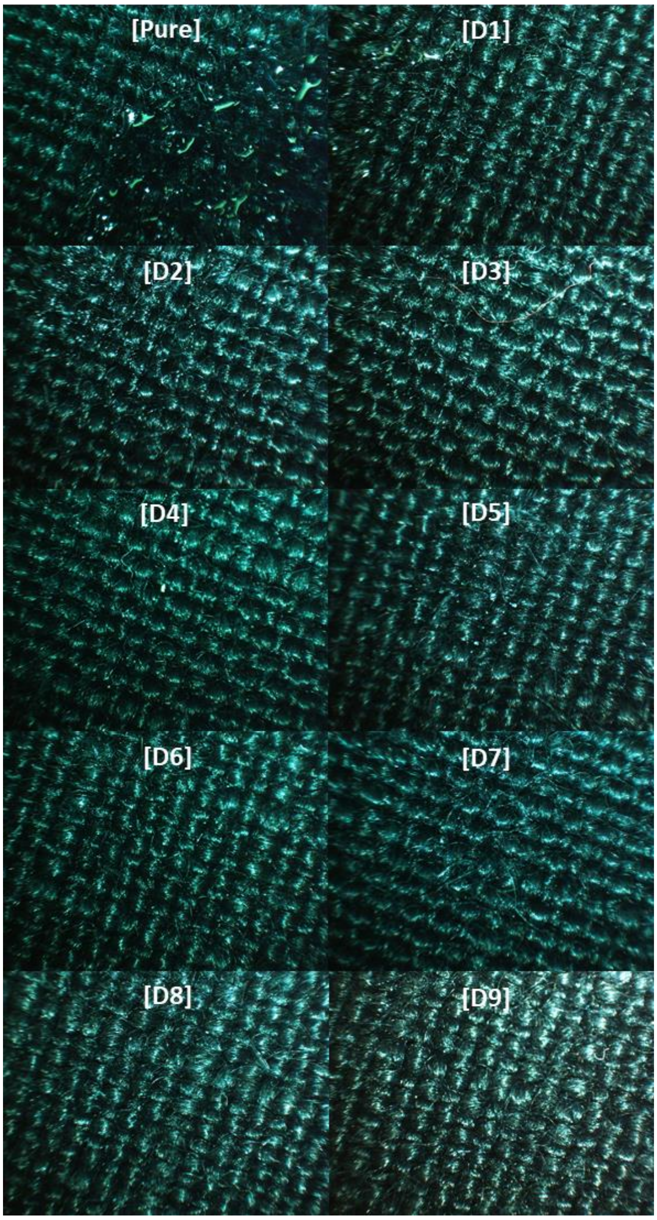


Figure 30. Images obtained with an optical microscope of the discoloration test performed with the concentrations described in Table 7.

4.4. <u>First Step:</u> One-Layer Fabric-Photolysis Decontamination-Best Condition Determination.

The first step of the experimental design was to determine the best condition for the photolysis experiment: type of lamp, time reaction and % of H_2O_2. For that, both the extract and the fabric were analyzed after the photolysis reaction, in order to determine the best removal of the PAHs tested with less fabric damage.

4.4.1. Extract Analysis.

Photolysis is a quite simple degradation route which can be very useful the pollutant absorbs at the same range that the energy source emits. As fire residues mostly consist of PAHs and aromatic compounds absorb in UV region, a lamp emitting below 400 nm may promote the degradation of these compounds[113].

Considering this, three conditions were evaluated: with UV lamp, with white lamp and without lamp (blank). To verify whether the lamps used could promote the degradation of PAHs, the emission spectra were obtained and are described in figure 31.

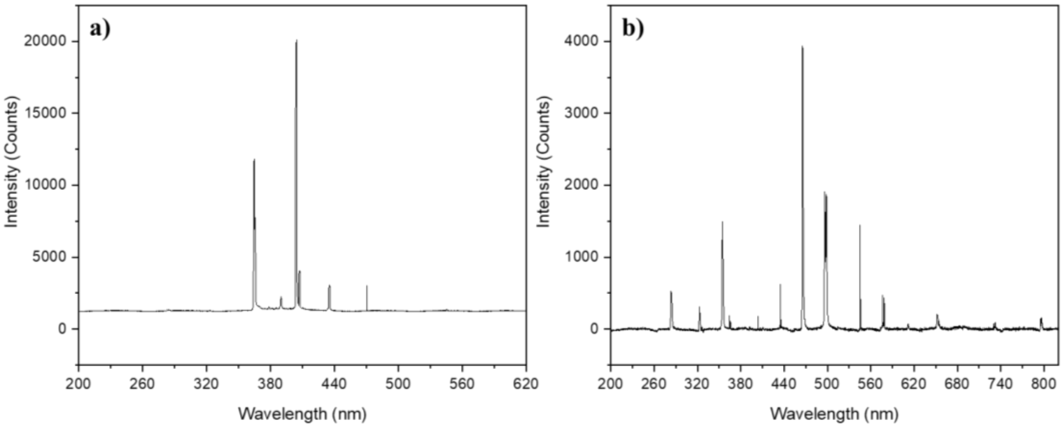


Figure 31. Emission spectrum of **(a)** mixed black lamp, Empalux® and **(b)** mixed white lamp, Luz Sollar®.

The ultraviolet lamp presents intense emissions at 360 nm and 404 nm, while the spectrum of the mixed white lamp presents several bands, both at lower wavelengths (283 nm, 322 nm, 353 nm) and at longer wavelengths (465 nm, 496 nm, 498nm, 545nm and 577nm). Comparing the emission spectra with the pollutant absorption spectra (Figure 32), the two lamps could be used to perform the photolysis of the materials. For this, a plan was elaborated, with variation of the energy source, H_2O_2 concentration and the reaction time.

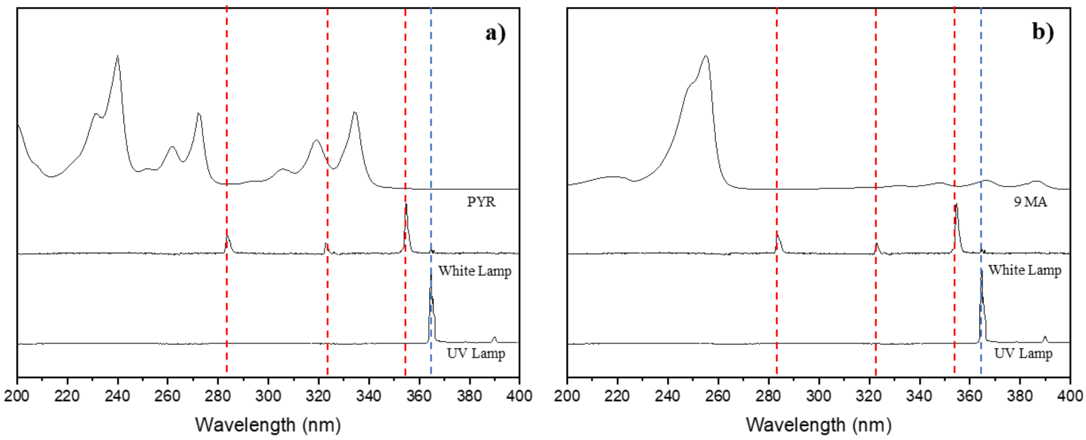


Figure 32. Comparison of emission spectrum of mixed black lamp, mixed white lamp and absorption spectra of compounds: **(a)** pyrene (PRY) and **(b)** 9-methylanthracene (9MA).

After carrying out the experiments, the degraded compounds were extracted with acetonitrile. This solvent was used both for deposition and extraction, as it has a low OH• radical removal effect, unlike other solvents (acetone, ethanol, methanol, 2-propanol, and others)[132,133], in addition to the analytes being soluble. The extracts were analyzed with UV/VIS and the spectra obtained are shown in Figure 33. When analyzing the UV/VIS spectra obtained without the use of a source of energy (BLK), the maximum degradation obtained was approximately 20±1%, using the longest reaction time - 3 days (Figure 33a). This reduction in concentration is probably related to the carryover of the analytes due to the airflow maintained inside the photoreactor. Photolysis experiments with only white lamp (WLP) (Figure 33d) and UV lamp (ULP) (Figure 33g) showed similar results, 65±9% and 57±2% for 1 day of decontamination, respectively. With 3 days of decontamination, 83±12% and 83±7%, for WLP and ULP, respectively. The addition of an oxidizing agent did not change the decontamination of contaminated fabrics. The decontamination percentage (Figure 29) are similar to the ones obtained without the use of hydrogen peroxide.

When comparing the results obtained with both lamps, one can see slightly better results using white lamp, especially for lower time (1 day). This fact can be related to the UV components observed in the white lamp, especially in the 250-270 nm region. In addition to the emission in regions of shorter wavelength, another possibility is that with the white lamp there is a formation of an intermediate radical with faster kinetics, which causes a greater degradation of 9MA in 1 day. When longer time is used, in both cases equilibrium seem to be achieved and maximum degradation is obtained no matter the lamp used (Figure 33d – f).

During the tests using the lamps, there was an increase in the photoreactor temperature, which remained around 35ºC - 40ºC. This may have favored the removal/ volatilization of pollutants rather than degradation. To evaluate this effect, an experiment was carried out inside an oven, without the use of an irradiation source (BLK + heat). The temperature used was 50ºC, the minimum of the equipment, and the results compared (Figure 34) with the percentages of removal obtained for the experiments in the dark and without heating (BLK).

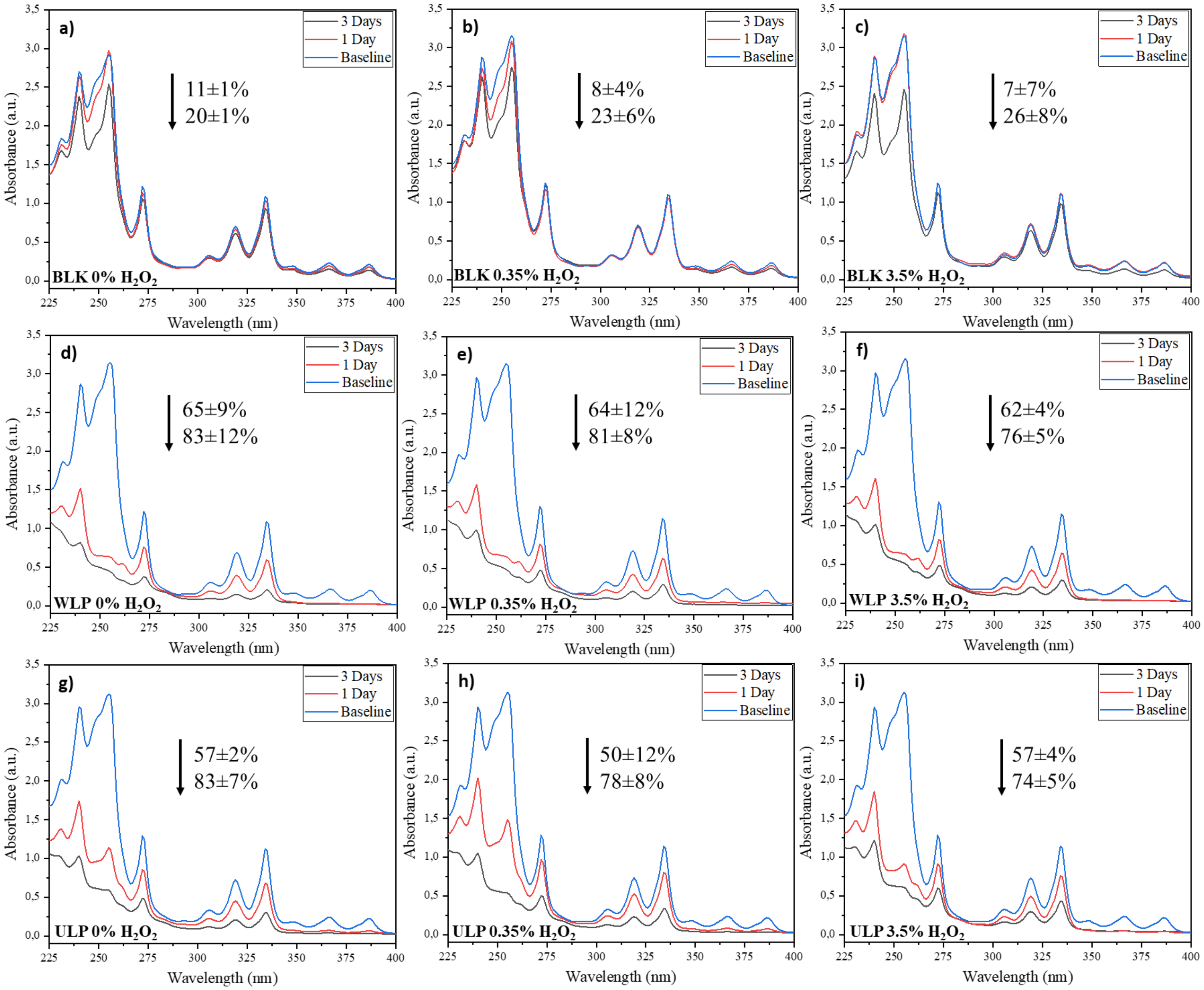
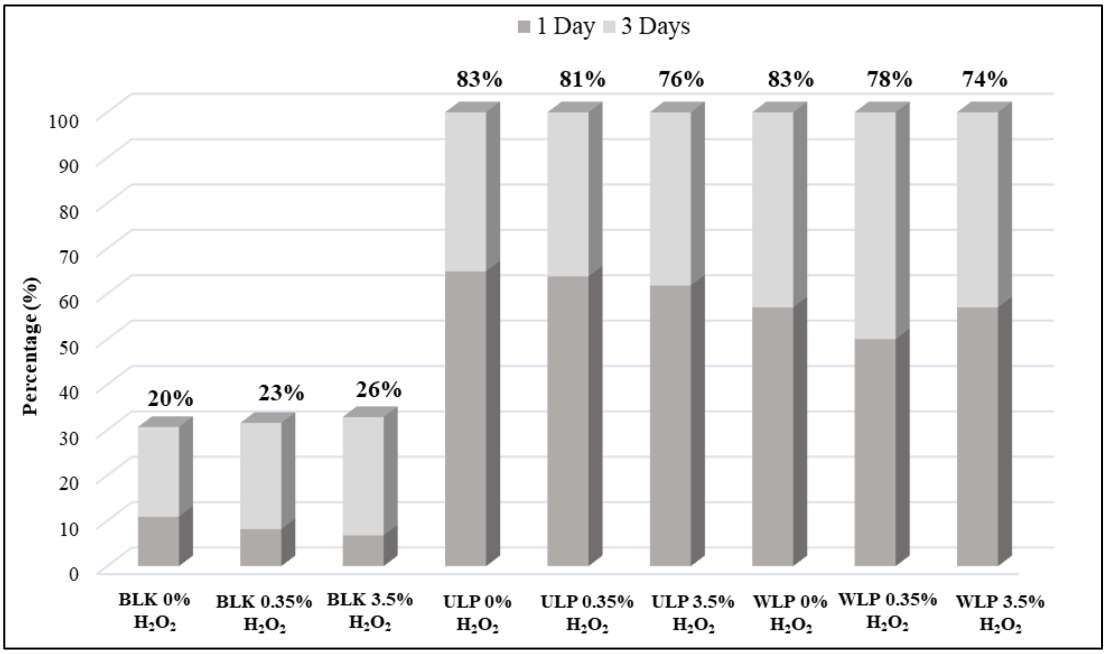


Figure 33. UV/VIS spectra of experiments performed in 1 and 3 days with **(a)** BLK 0% of H_2O_2, **(b)** BLK 0.35% of H_2O_2, **(c)** BLK 3.5% of H_2O_2, **(d)** WLP 0% of H_2O_2, **(e)** WLP 0.35% of H_2O_2, **(f)** WLP 3.5% of H_2O_2, **(g)** ULP 0% of H_2O_2, **(h)** ULP 0.35% of H_2O_2 and **(i)** WLP 3.5% of H_2O_2.



Graph 29. Removal percentage of PAH after the experiments performed in 1 and 3 day with BLK 0% of H_2O_2, BLK 0.35% of H_2O_2, BLK 3.5% of H_2O_2, WLP 0% of H_2O_2, WLP 0.35% of H_2O_2, WLP 3.5% of H_2O_2, ULP 0% of H_2O_2, ULP 0.35% of H_2O_2 and ULP 3.5% of H_2O_2.

In this case, a decontamination of 59±18% of the compounds (versus 20±1% at room temperature) was obtained after 3 days, indicating that temperature is a factor that favors removal/volatilization of the analytes studied. However, using lamps removal percentages as high as 83% were achieved, also, the temperature obtained when using the lamps were lower than 50ºC. Considering these facts, we can consider that the PAHs are being degraded, not only being volatilized.

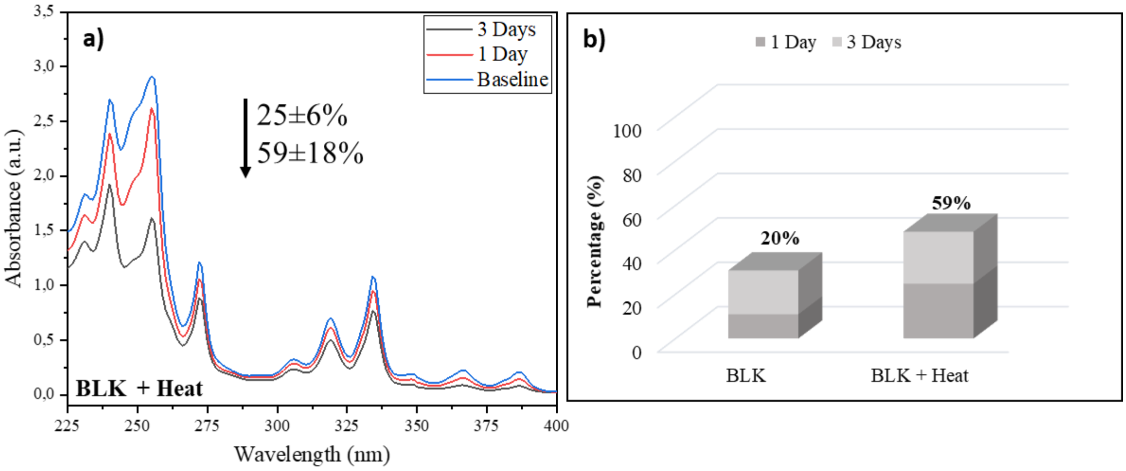


Figure 34. (a) UV/VIS spectra of the photolysis tests performed in the test with heating and **(b)** degradation rates of the experiments BLK and BLK + heating.

4.4.2. Fabric Analysis.

An important factor that must be considered when determining a PFPC decontamination technique is the integrity of the fabric fibers after the procedure. For this, the treated fabrics (**without the analytes**) were analyzed by infrared spectroscopy with attenuated total reflection Fourier transform, tearing strength, optical microscopy and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy. The fabrics treated for 3 days with BLK 0% of H_2O_2, BLK 0.35% of H_2O_2, BLK 3.5% of H_2O_2, WLP 0% of H_2O_2, WLP 0.35% of H_2O_2, WLP 3.5% of H_2O_2, ULP 0% of H_2O_2, ULP 0.35% of H_2O_2 and ULP 3.5% of H_2O_2 were analysed.

4.4.2.1.Optical microscopy.

Images of the virgin fabrics and of the treated fabrics (without the analytes) were obtained with the aid of an optical microscope (Figure 35) to qualitatively characterize the fabric surface. When analyzing the images, it was not possible to observe changes in the fibers or in the color of the fabric. Thus, it can be concluded that the decontamination carried out did not promote fiber degradation, maintaining the integrity of the fabrics.

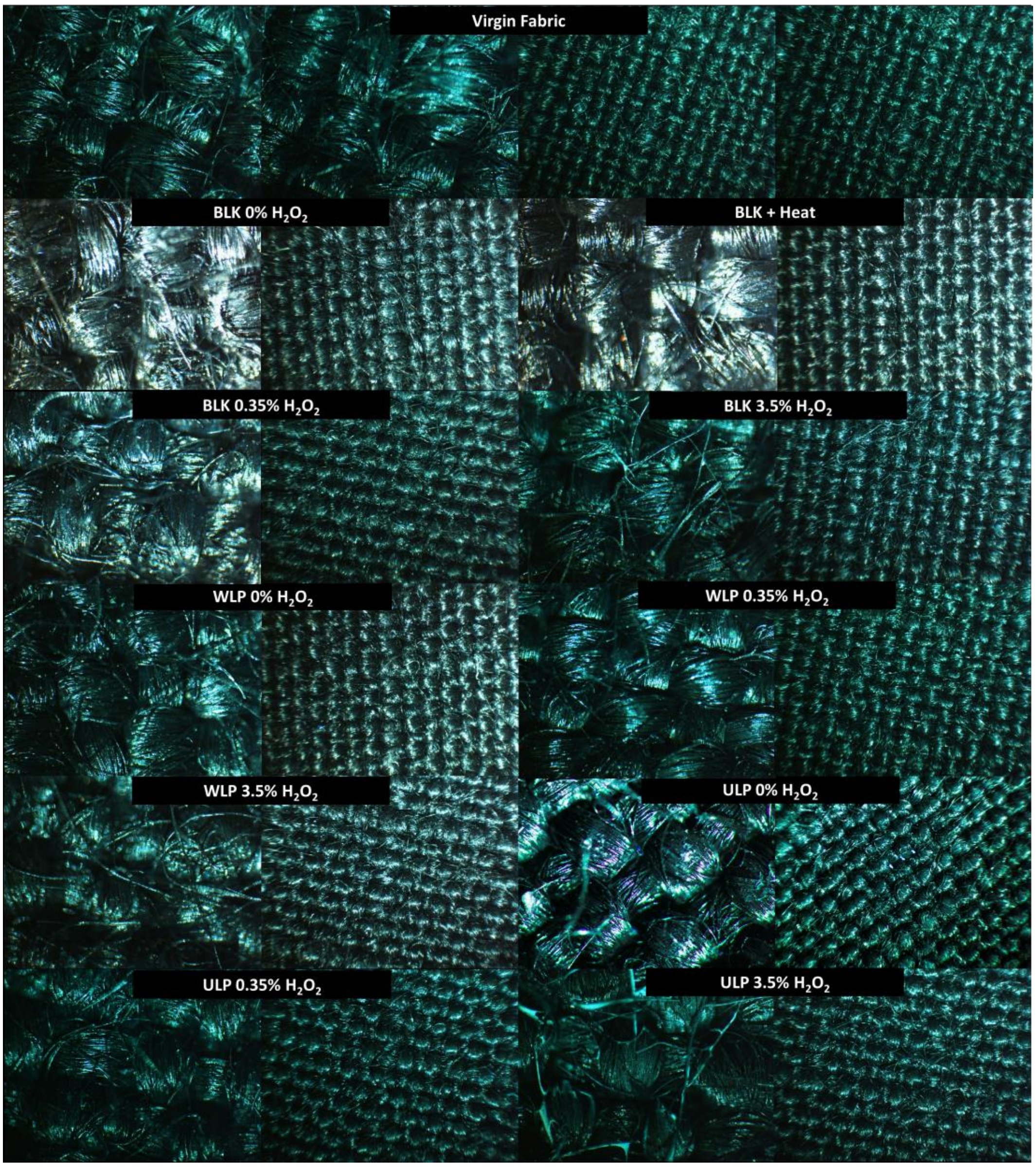


Figure 35. Images of fibers before (virgin fabric) and after treatment: BLK 0% of H_2O_2, BLK 0.35% of H_2O_2, BLK 3.5% of H_2O_2, WLP 0% of H_2O_2, WLP 0.35% of H_2O_2, WLP 3.5% of H_2O_2, ULP 0% of H_2O_2, ULP 0.35% of H_2O_2 and ULP 3.5% of H_2O_2.

4.4.2.2.SEM.

SEM micrographs of outer shell fabric were obtained to visualize the morphology of the fibers, searching for possible alterations. Images were obtained before decontamination – **untreated** (Figure 36) and after decontamination for 3 day (Figure 37). The diameters and standard deviations are described in Table 18. The micrographs did not show any change in fabric morphology, and the fibers had similar diameters, within the standard deviation. Thus, the results suggest that there were no changes in the fabric surface and the fibers maintained their structure.

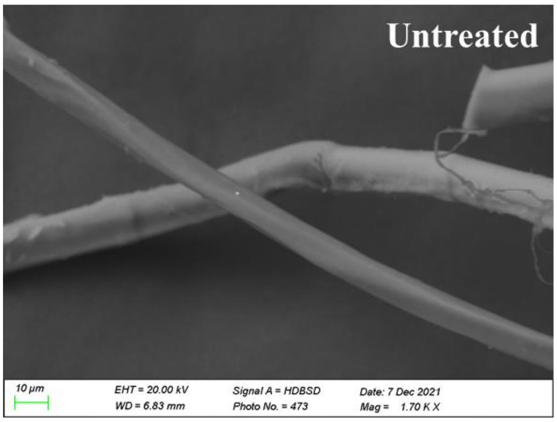


Figure 36. Micrographs of fibers before treatment - **untreated**.

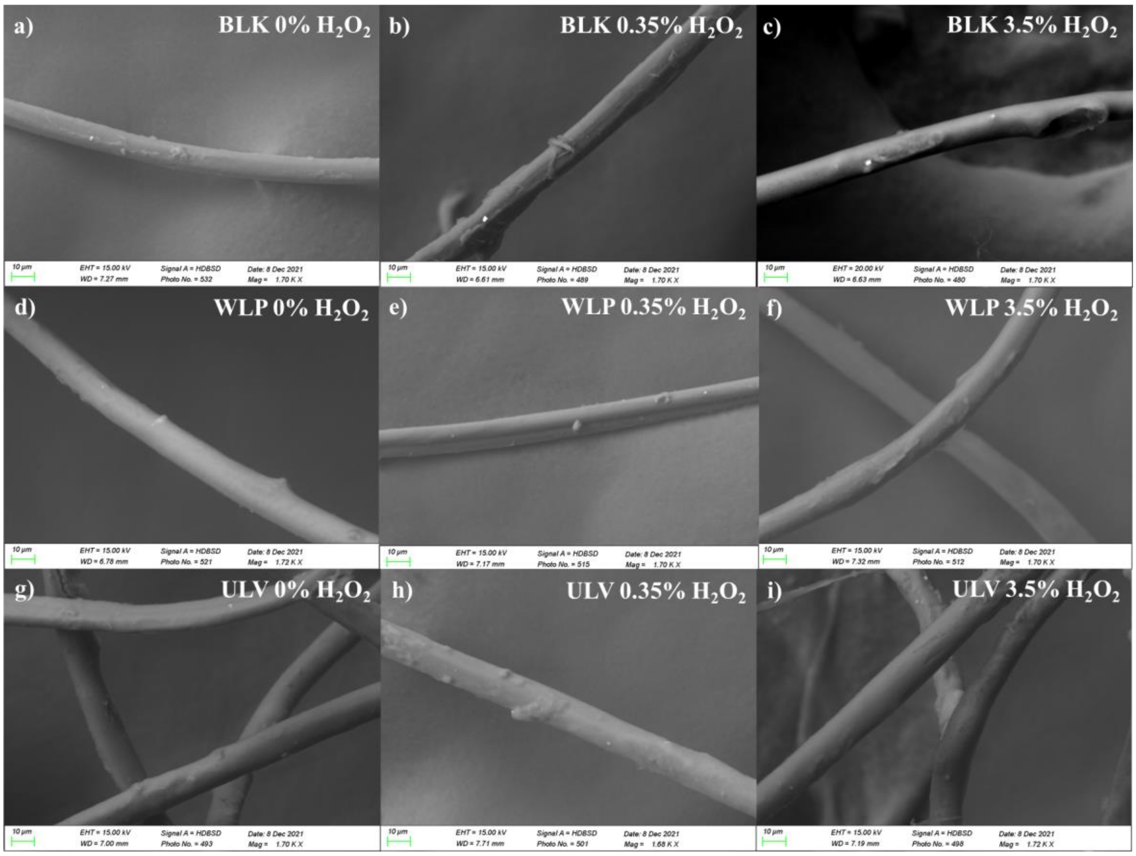


Figure 37. Micrographs of fibers after treatment **(a)** BLK 0% of H_2O_2, **(b)** BLK 0.35% of H_2O_2, **(c)** BLK 3.5% of H_2O_2, **(d)** WLP 0% of H_2O_2, **(e)** WLP 0.35% of H_2O_2, **(f)** WLP 3.5% of H_2O_2 **(g)** ULP 0% of H_2O_2, **(h)** ULP 0.35% of H_2O_2 and **(i)** ULP 3.5% of H_2O_2.

In a similar study carried out by Davis *et al.* [134] in which outer shell fabrics used in firefighter jacket and pants were exposed to simulated ultraviolet sunlight at 50ºC and 50% relative humidity for several periods of time. The experiments were carried out in the NIST SPHERE (Simulated Photodegradation via High Energy Radiant Exposure), a simulated photodegradation device. In confocal microscope images obtained by the group, Figure 38, it was possible to observe fiber degradation after fabric exposure to simulated sunlight. The study observed that there was surface corrosion and fiber shape deformation after 13 days of treatment. It is worth mentioning that the experiment carried out by the group used an experimental scheme different from that described in this thesis, considering that the wavelength used presents emission from the region of 360 nm.

Table 18. Fiber diameter

Sample	*Mean (μm)*	*Standard deviation (μm)*
Untreated	14.15	2.71
BLK 0%	13.90	1.50
BLK 0.35%	13.68	1.19
BLK 3.5%	14.35	1.62
WLP 0%	14.00	2.57
WLP 0.35%	14.36	1.26
WLP 3.5%	13.85	1.95
ULP 0%	13.52	1.35
ULP 0.35%	14.38	1.04
ULP 3.5%	13.39	1.34

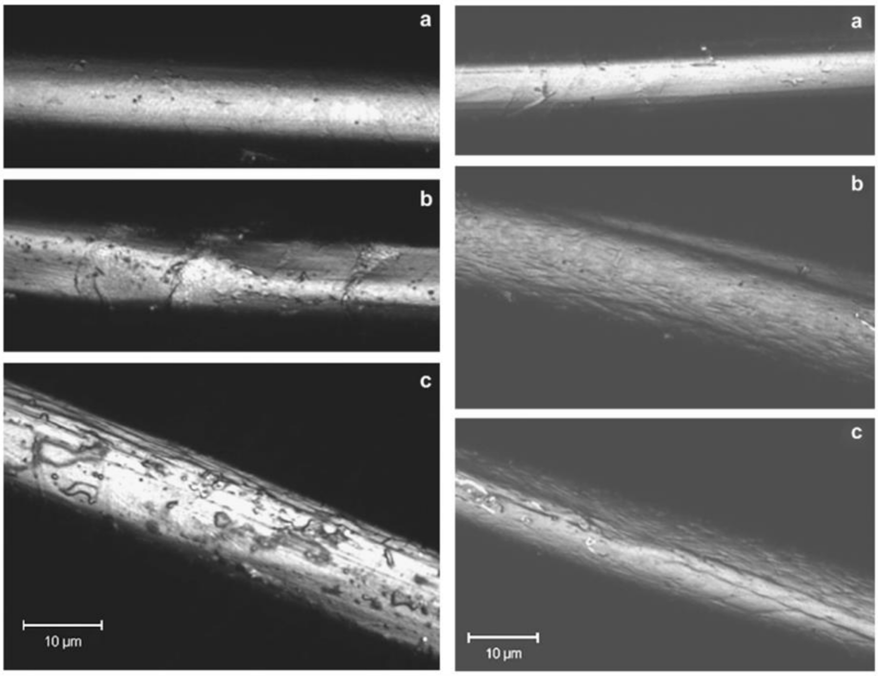


Figure 38. Confocal microscope images of Kevlar (left) and Nomex (right) fibers after **(a)** 0 d, **(b)** 13 d, and **(c)** 66 d of UV irradiation obtained by Davis *et al.* [134].

4.4.2.3.FTIR/RTA.

One method applied to assess the integrity of the fibers was the FTIR/RTA as performed by Davis, *et al.*[134]. With the analysis by FTIR/RTA it is possible to verify if chemical changes occur after the decontamination of the fabric. The fabric is made up of a mixture of Nomex® (meta-aramid) and Kevlar® (para-aramid) substances, which can undergo oxidation, forming acids, alcohols and/or amines[134–136] (Figure 39).

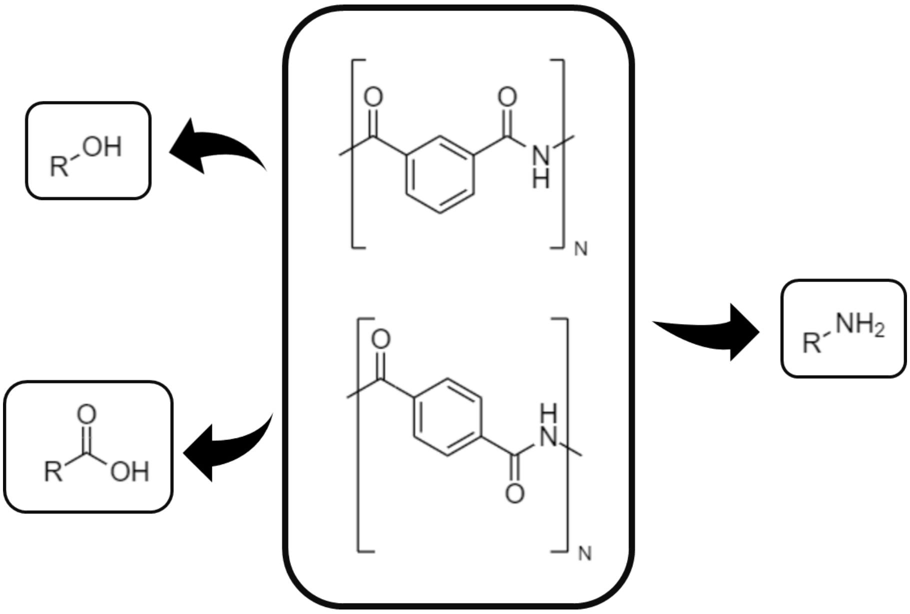


Figure 39. Degradation of Nomex® and Kevlar® fibers forming acids, alcohols and amines.

In case of fabric degradation, it would be possible to observe a reduction in the intensity of the amide bands and an increase in the intensity of the bands in the region of O-H and N-H. The FTIR spectra of virgin fabric were compared with fabric after treatment (Figure 40), and no reduction or appearance of new bands was observed.

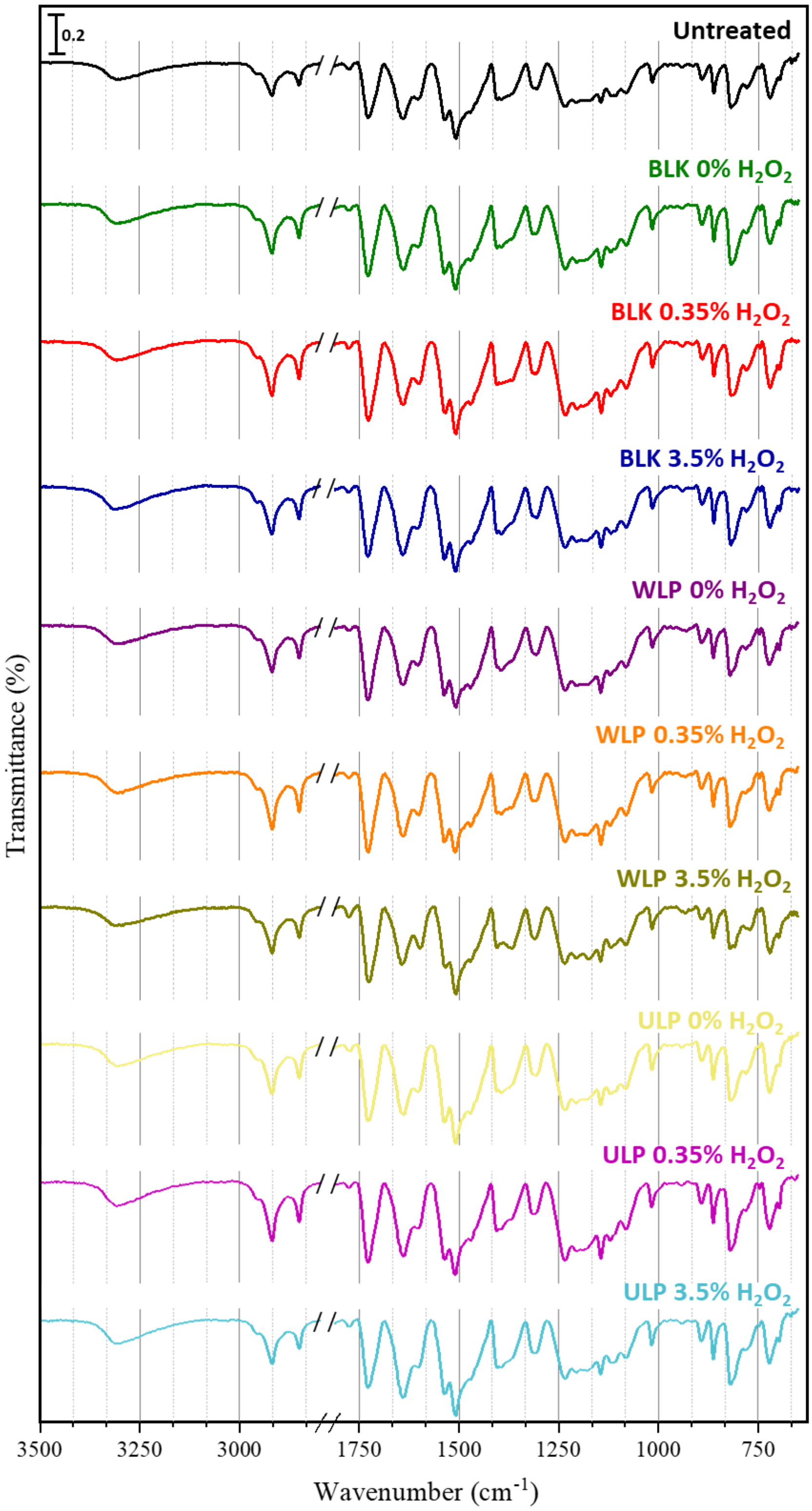


Figure 40. FTIR/RTA spectra of untreated sample and treated samples for 3 days: BLK 0% of H_2O_2, BLK 0.35% of H_2O_2, BLK 3.5% of H_2O_2, WLP 0% of H_2O_2, WLP 0.35% of H_2O_2, WLP 3.5% of H_2O_2, ULP 0% of H_2O_2, ULP 0.35% of H_2O_2 and ULP 3.5% of H_2O_2.

The band at 3307 cm^{-1} refers to the N-H stretch of the amide of the para-aramid and meta-aramid compounds, and the band at 1724 cm^{-1} refers to the C=O stretch. Because the fact that the fibers present aromatic rings, it is possible to identify the C=C aromatic stretch at 1640 cm^{-1}. The region at 1017 – 820 cm^{-1} corresponds to the C-H out-of-plane vibration, indicating a meta and para substitution. The bands in the range 2918 – 2850 cm^{-1} are characteristic of C-H sp^3 stretching. However, fiber do not have saturated carbons, so the bands must come from the water repellant coating. For the Unishell®, the outer shell fabric receives a fluorocarbon (Teflon®) coating, which guarantees the repellency characteristic. The other attributions of the bands are described in Table 19 and are in accordance with what is described in the literature[134,136,137].

Table 19. Assignment of FTIR/RTA bands.

Band (cm^{-1})	***Assignment***
3307	N-H stretch
2918 - 2850	C-H sp^3 stretch
1724	C=O amide stretch
1640	C=C aromatic stretch
1537 - 1472	N-H deformation in plane and C-N stretch
1411 e 1304	C-N aromatic stretch
1017 - 820	C-H vibration out-of-plane

Thus, the treatments applied to the fabrics using a source of light and H_2O_2 allowed the degradation of the deposited PAHs without evidence of alterations the chemical structure of fibers.

Considering that the WLP promoted the best results and H_2O_2 showed to be indifferent in the concentration tested, and that no changes were observed during the fabric analysis, **it was chosen as best condition the use of WLP for 3 days, without H_2O_2 or heat** – and it was used to decontaminate PAHs from firefighters' protective clothing. Considering that, the next steps of the experimental design were carried out. First, the photolysis by-products and kinetics in only one layer of fabric was obtained and, after, an efficiency test employing in all three layer was conducted.

4.5. <u>Second Step:</u> One Layer-Fabric-Photolysis-By-Products.

By-products formed after WLP and 0% H_2O_2 decon of turnout outer shell were determined by GC/MS. Initially, extracts from virgin fabric (**without the addition of analytes**) were evaluated. With the mass spectrum (Figure 41), it was possible to determine the structure of the compounds extracted. It was possible to determine the presence of compounds: 1,3-dimethyl-2-imidazolidinone, 2,4-Di-tert-butylphenol, N,N-diethyl-4-methyl-Benzamide, N,N-dimethyloctadecan-1-amine, Hexadecanamide and (Z)-9-octadecenamide. The compounds found are derived from the polymers used in the manufacture of Kevlar® (para-aramid) and Nomex® (meta-aramid) fiber. In addition, long-chain aliphatic compounds were also identified. These come from the product used as a waterproofing agent in the fabrics, which may have reacted with the fabric and/or solvent used during the extraction stage.

The main by-products of degradation expected by direct photolysis are ketones, hydroxylated compounds and reaction products of the parent compound with singlet oxygen[124]. For pyrene, the compounds 1-hydroxypyrene (Figure 42a), 1,8-pyrenedione (Figure 42b), 1,6-pyrenedione (Figure 42c) and 4H-cyclopenta[def]phenanthrene-4-one (Figure 42d) are described in the literature as by-products of the photolysis reaction[138]. As for 9-methylanthracho PAH, the literature describes the compounds as by-products: phenanthrene-9,10-dione (Figure 43a), anthraquinone (Figure 43b), dibenz[b,e]oxepin-11(6H)-one (Figure 43c) and 2-acetylbenzoic acid (Figure 43d)[139].

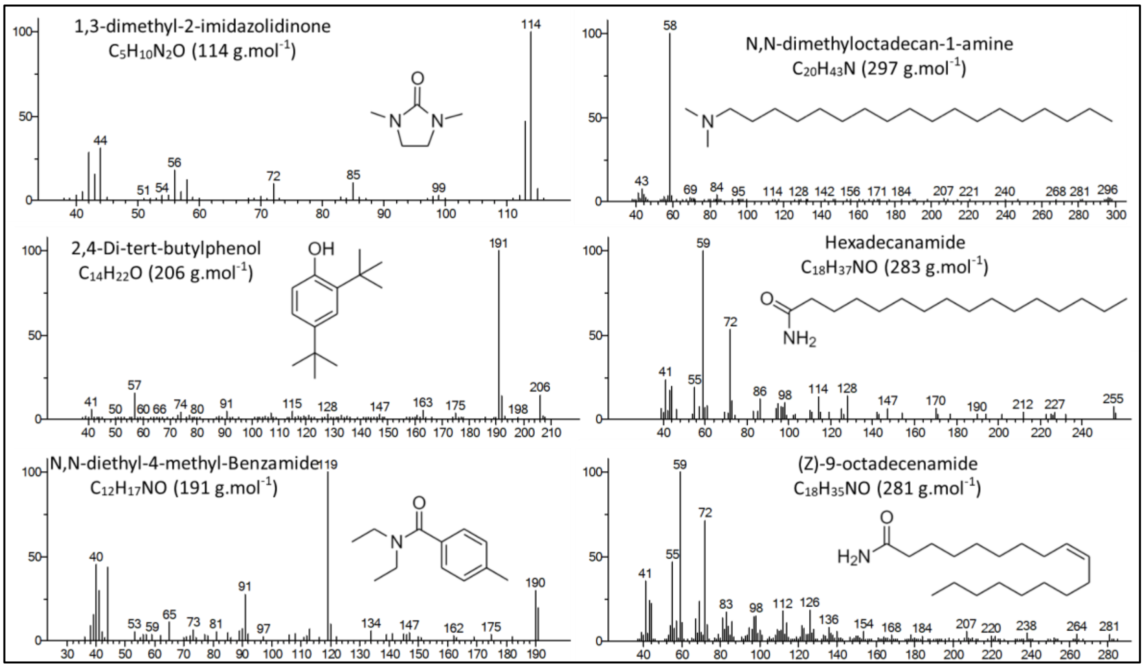


Figure 41. Mass spectrum of compounds extracted from virgin fabric.

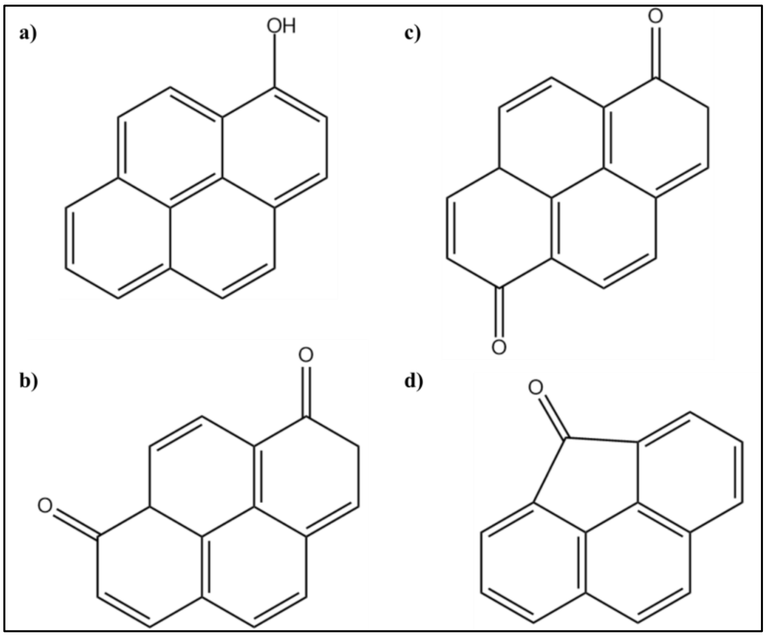


Figure 42. Expected by-products of the photolysis degradation of pyrene: **(a)** 1-hydroxypyrene, **(b)** 1,8-pyrenedione,**(c)** 1,6-pyrenedione and **(d)** 4H-cyclopenta[def]phenanthrene-4-one[138].

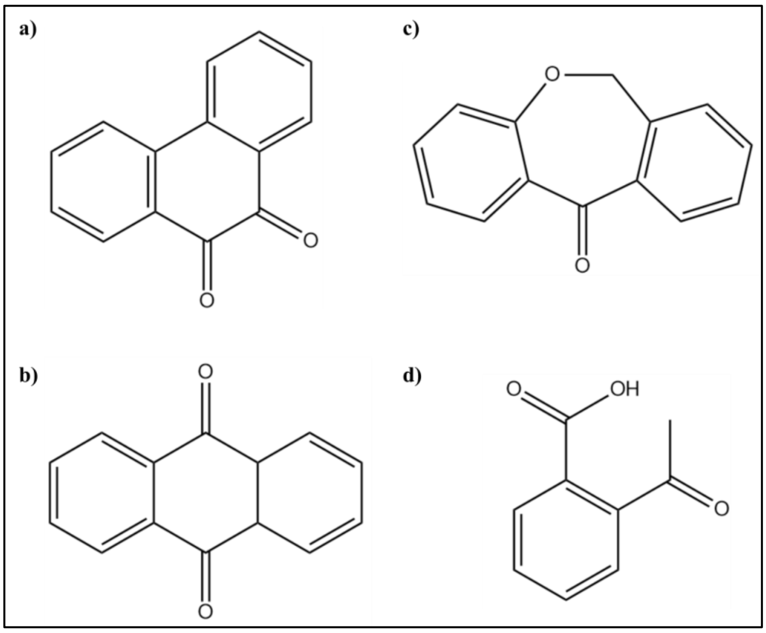


Figure 43. Expected by-products of the photolysis degradation of 9-methylanthracene: **(a)** phenanthrene-9,10-dione, **(b)** anthraquinone, **(c)** dibenz[b,e]oxepin-11(6H)-one and **(d)** 2-acetylbenzoic acid[139].

Extracts from WLP 0% H_2O_2 experiments (0, 1, 3, 6, 9, 12 and 15 days) were also analyzed by GC/MS and compared with fabrics without treatment (baseline). The compounds identified after decontamination can be considered as by-products of the degradation of the PAHs used. In Figure 44 it is possible to identify the peaks referring to the new structures. All chromatograms are attached in the appendix.

By analyzing the mass spectrum obtained at 21.529 min (Figure 45a) it was possible to determine that the by-product would be the compound 3,4-dihydro-4-phenyl-2H-1-benzopyran-2-one, with the molecular ion visible ($M^{+\bullet}$) of 224 *m/z* and the base peak of 181 *m/z*, corresponding to the loss of C_2H_3O. The peak at 23.593 min (Figure 45b) corresponds to the compound 9,10-Anthracenedione, a by-product of 9-methylanthracene. It was also possible to identify the molecular ion (M+•) with 208 *m/z* and it´s fragments in 180 *m/z* (loss of CO), 152 *m/z* (loss of two CO) and 76 (loss of C_6H_4). A peak at 24.133 min (Figure 45c) corresponds to the Methyl 2-benzoylbenzoate, possibly derived from 9,10-anthracenedione. The molecular ion ($M^{+\bullet}$ 240 *m/z*) presents low intensity, because of its high reactivity. The base peak has 209 *m/z*, corresponding the loss of CH_3O. Other fragments are: 194 *m/z* (loss of CH_3O and O), 178 *m/z* (loss of CH_3O and two O), 165 *m/z* (loss of $C_2H_3O_2$ and O), 152 *m/z* (loss of $C_2H_3O_2$ and CO) and 76 *m/z* (loss of $C_9H_8O_3$). Finally, the peak at 24.224 min (Figure 45c) corresponds to 1a,9b-dihydro- 1H-Cyclopropa[l]phenanthrene, possibly from pyrene analyte. The parental molecular ion at 192 m/z has higher intensity, being very stable. It´s fragments are: 178 (loss of CH_2), 165 (loss of C_2H_3) and 152 (loss of C_3H_4). All four by-products formed during the reaction had a higher concentration after 1 day reaction and decreased with the course of the reaction, being also consumed by the photolysis reaction.

The degradation mechanism of pyrene and 9-methylanthracene analytes are different from the compounds described in Figures 42 and 43. This fact was expected, considering that the degradation was carried out in a different matrix from the studies described in the literature and the experiment was carried out with the mixture of the two PAHs, and reactions between the generated by-products may occur. However, the structures formed, typically alcohols and esters, are similar, showing consistency with the likely mechanism of OH▪ addiction.

Despite the existence of organic by-products, indicating that there was no total mineralization of the analytes, it is important to emphasize that the products found have greater solubility in water than the parent compounds, facilitating their removal. Regarding the toxicity of these products, these data are not available in the literature, and further studies are needed[140].

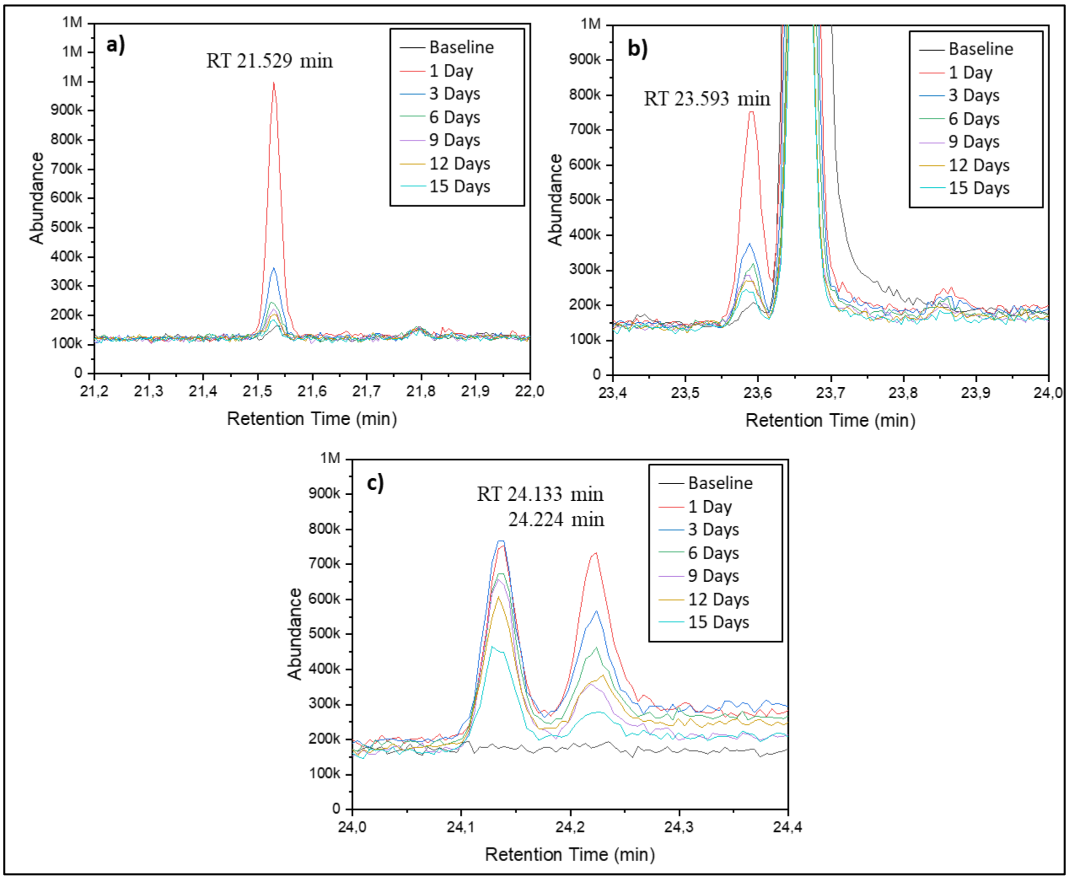
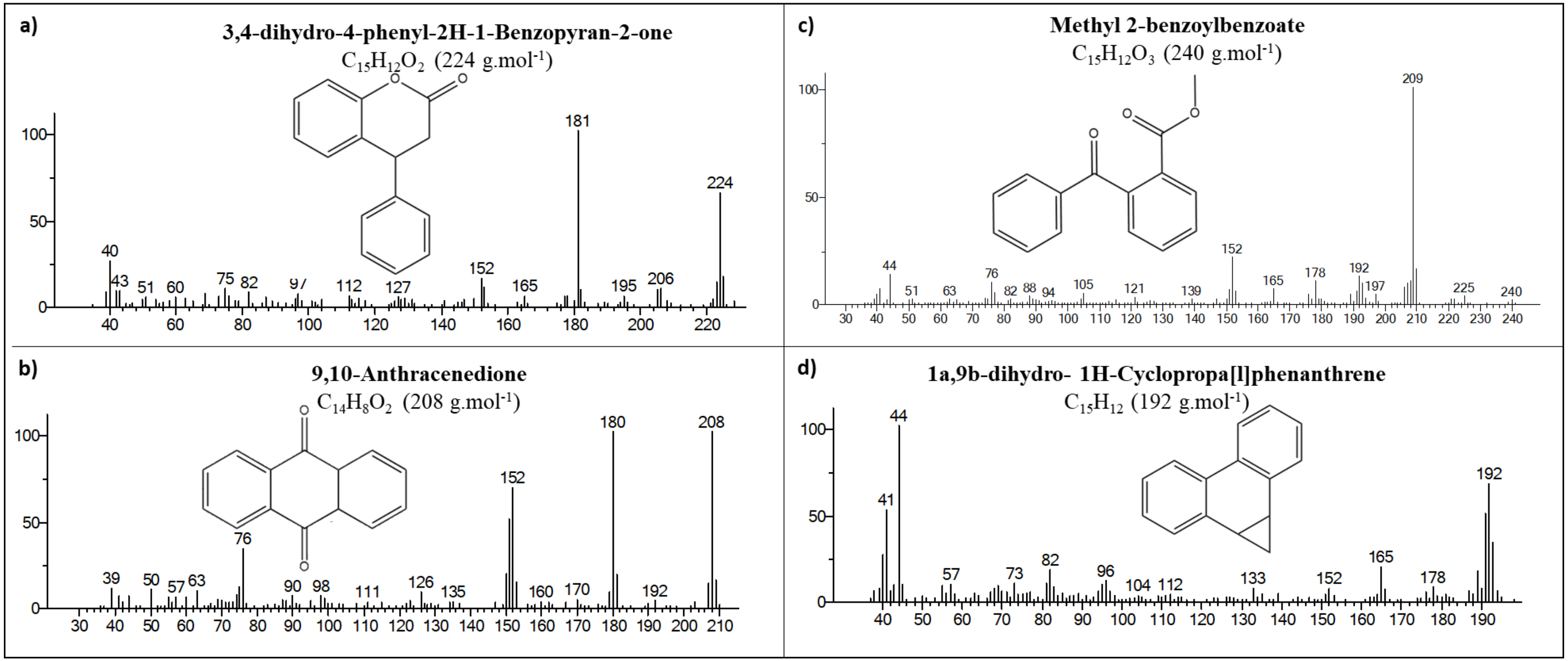


Figure 44. Chromatograms of by-products found after white lamp photolysis in the retention time of **(a)** 21.529 min, **(b)** 23.593 min and **(c)** 24.133 and 24.224 min.



a) **3,4-dihydro-4-phenyl-2H-1-Benzopyran-2-one**
$C_{15}H_{12}O_2$ (224 g.mol^{-1})

b) **9,10-Anthracenedione**
$C_{14}H_8O_2$ (208 g.mol^{-1})

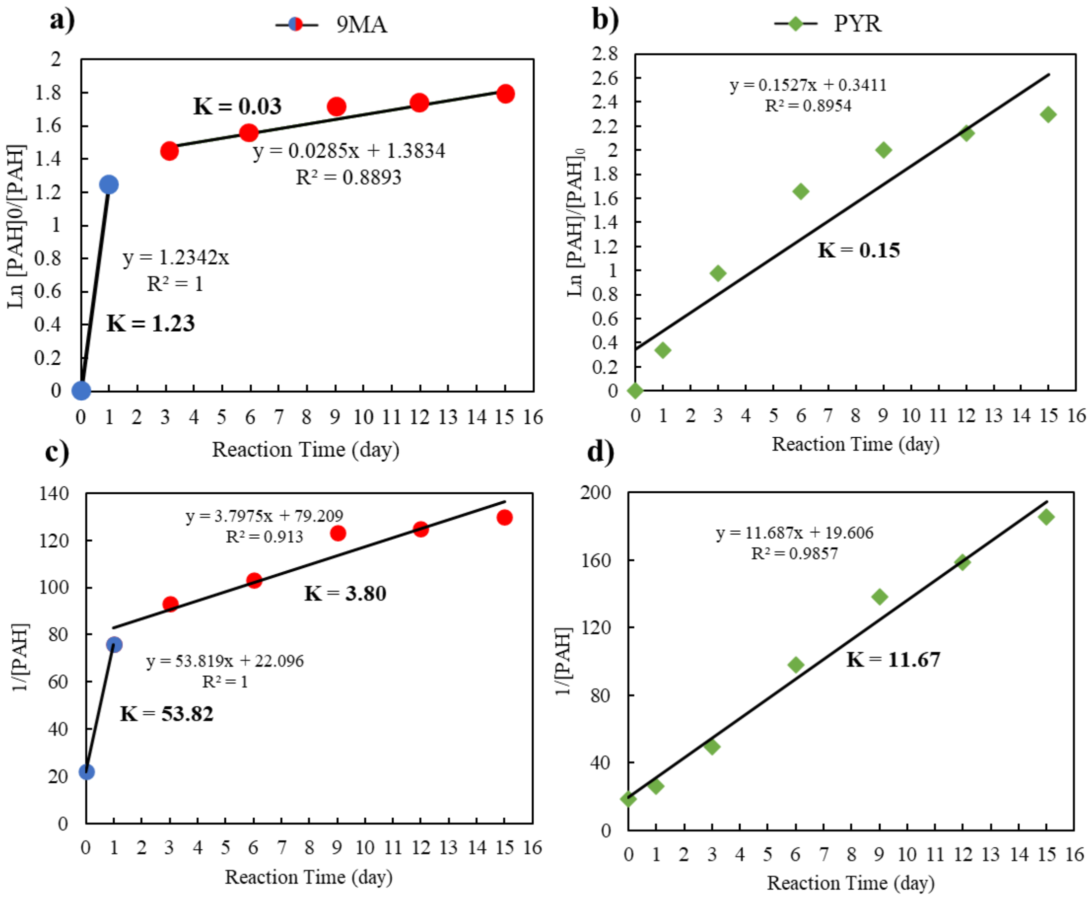
c) **Methyl 2-benzoylbenzoate**
$C_{15}H_{12}O_3$ (240 g.mol^{-1})

d) **1a,9b-dihydro- 1H-Cyclopropa[l]phenanthrene**
$C_{15}H_{12}$ (192 g.mol^{-1})

Figure 45. Mass spectra at retention times **(a)** 21.529 min, **(b)** 23.593 min, **(c)** 24.133 min and **(d)** 24.224 min of the by-products found after white lamp photolysis

4.6. Third Step: One Layer-Fabric-Photolysis-Kinetics

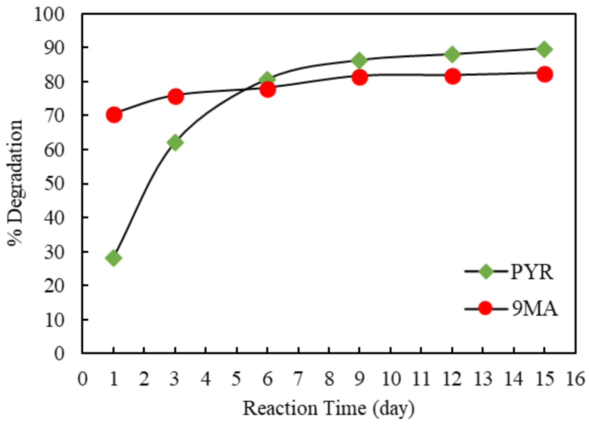
The kinetics of the best photolysis condition (WLP 0% of H_2O_2) were determined and for that the extracts obtained were analyzed with **GC/MS**, rather than with UV/Vis. This was done so that the kinetics of each PAH photolysis reaction were found. Two models were considered, pseudo-first order and pseudo-second order kinetics. The linear regression of the plots Ln([PAH]/[PAH]$_0$) versus reaction time (pseudo-first-order) and 1/[PAH] versus reaction time (pseudo-second-order) were used in order to determine the reaction kinetics (Graph 30). The white lamp-photolysis removal of the compounds 9-methylanthracene and pyrene follows a pseudo-second-order reaction, which presented a better fitting with a higher R-squared.



Graph 30. Degradation kinects determination for PYR and 9MA: pseudo first order fitting **(a)** and **(b)**, pseudo second order rate **(c)** and **(d)**.

For the pseudo second fitting, the degradation of 9-methylanthracene follows two step kinetics: initially a faster reaction, with a rate constant of 53.82 L.mol^{-1}.s^{-1}, and then a slower kinetic, with constant of 3.80 L.mol^{-1}.s^{-1}. This two-step reaction, in which the first one is quite fast, explains the result previously obtained, which shows a greater degradation of 9MA after only 1 day of irradiation. According to Zhao, S., *et al.*[141] PAHs with higher molecular masses have greater reactivity. In the case of alkyl-substituted PAHs, these are more photoreactive than the unsubstituted ones. PAH 9-methylanthracene shows greater reactivity[139] and faster degradation than pyrene.

Pyrene, on the other hand, has a monotonic behavior with a constant rate k of 11.67 $L.mol^{-1}.s^{-1}$ throughout the reaction time. The efficiencies obtained throughout the test are described in Graph 31. After 3 days of reaction, was obtained a removal of both PAH above 60% and 70%. After 6 days of decontamination, there is an equality in the removal percentage of both analytes. Considering the cost-benefit ratio, the 3 days time was adopted as optimal, considering that the gain from the 3rd to the 6th day is very small compared to the cost.



Graph 31. WLP 0% of H_2O_2 efficiencies obtained in 0, 1, 3, 6, 9, 12 and 15 days.

The difference between the degradation rates determined by the GC and UV/VIS techniques (described in topic **4.4.**) is related to the fact that, with this technique, all compounds that absorb in the region are considered in the calculation and may include some compound that is not related to the analytes. Therefore, the % obtained by gas chromatography are more accurate, as it is possible to analyze the concentration of the specific compound, unlike the UV/VIS technique, where the analysis is made of all compounds that absorb in the analyzed region.

4.7. <u>Fourth Step:</u> One Layer-Fabric-30 Days Photolysis Fabric Analysis.

In this step, the fiber analysis was performed in a sample obtained after 30 days exposure test using the best reaction condition (lamp type and % H_2O_2 – WLP with 0% H_2O_2) determined in previously experiments. This decontamination time was used so that the analysis was obtained after a longer exposure time, which would promote greater wear of the fabric fibers. As were performed previously, the FTIR/RTA spectra obtained no treatment was compared to the one obtained after the long exposure experiment (Figure 46). Again, no big changes were visualized, that can indicate the fiber degradation.

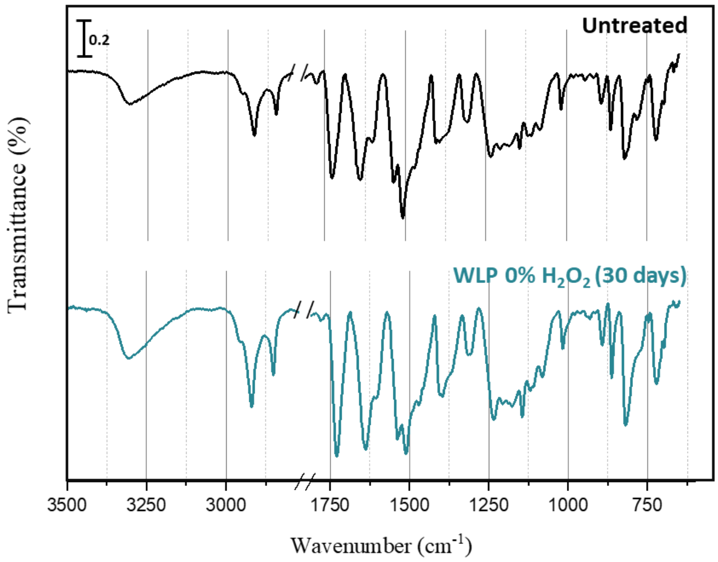


Figure 46. FTIR/RTA spectra of untreated fabric and fabric treated with WLP 0% of H_2O_2 performed for 30 days.

Another way to assess changes in fabric construction and possible wear from the decontamination process is by performing a tearing strength test, as described in NIST report 1751[135]. Specifically for the firefighting protective clothing, the NFPA 1971[142] standard (item 7.1.11) determines the necessity of a tear resistance greater than 100N for the outer layer of combat suits.

In the test performed (Table 20) with the Unishell® fabric (composed of 58% kevlar®, 40% nomex® and 2% carbon), the tearing strength values of 260.97±10.10N and 218.39±28 80N were obtained for warp and weft, respectively. After the decontamination process with white lamp photolysis, tearing strength values of 192.62±31.80N and 181.52±22.90N were obtained for warp and weft, respectively.

Table 20. Tearing strength (N) values with expanded uncertainty with 95% confidence, performed in accordance with ASTM D2261[126].

	Warp	***Weft***
Before 30 days WLP decon	260.97±10.10	218.39±28.80
After 30 days WLP decon	192.62±31.8	181.52±22.9
ΔN(absolute)	68.35	36.87
ΔN(%)	26%	17%

Horn *et al.*[76] identified a reduction in tearing strength tests after washing. The group evaluated the three layers of fabric and three methods of decontamination: laundering, brushing with soapy water and dry brushing. Regarding the laundering technique in the washing machine and the external fabric, after 10 washes, there was a reduction of 1.2% - 9.1%. With 20 washes, the reduction was 9.3% - 19.6% and with 40 washes, it was 24.1% - 41.1%. For fabrics that were laundered in the washing machine, the tear strength dropped below 100 N, a minimum requirement per NFPA 1971120. With WLP, there was a reduction of 17% - 26%. This value can be related to the breaking of the bonds of the fabric's water repellant coating, and not necessarily due to fiber degradation, as described by Davis *et al.*[134], A fact that corroborates this assertion is that no alterations were observed in the FTIR/RTA spectra, indicating the breaking of the bonds of the para-aramid and meta-aramid molecules. In Davis experiment with Kevlar® and Nomex® outer shell fabrics irradiated with sunlight, after 18 days of exposure, a 40% reduction in fabric strength was observed, a greater reduction than the one observed in or experiments.

Also, in the experiments performed by Davis *et al*,.[134] was possible to visualize fiber degradation with confocal microscope, as shown previously in Figure 40. Opposed that, in our experiments, the SEM micrographs obtained after 30 days photolysis (Figure 47) no changes were identified in fabric morphology, and in the fiber diameter (FDM) - 14.53±1.80 μm. Again, this result supports the idea that the reduction in tearing strength previously described is associated to the Teflon® water repellant coating.

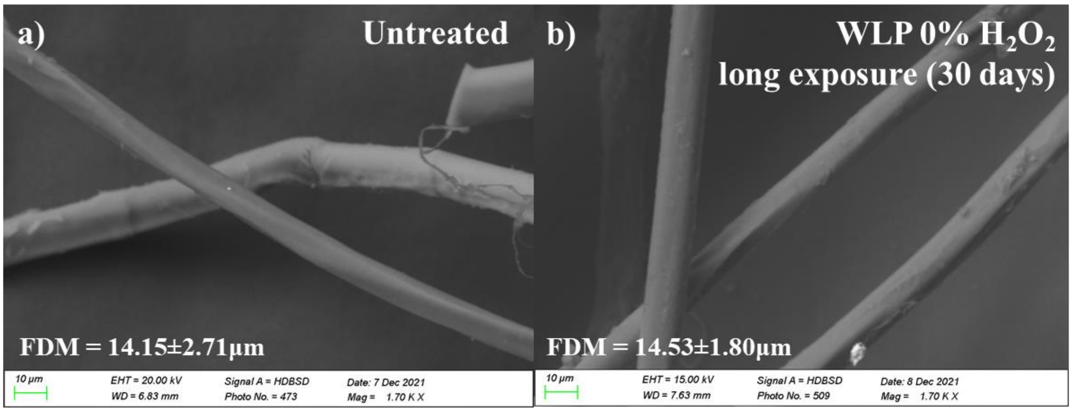


Figure 47. Micrographs of fibers after treatment WLP 0% of H_2O_2 for 30 days.

To confirm the thesis that white lamp photolysis is only removing layer from the fabric, fluorine element maps were obtained with scanning electron microscopy coupled to energy dispersive X-ray spectrometry (Figure 48). This was done because Teflon® is fluorine-containing polymer and, with SEM/EDS, it is possible to verify its distribution on the surface of the fiber. It is important to mention that the Raman spectroscopy and Atomic Force Microscopy techniques were also tested at this stage of the work, however, it was not possible to obtain any results due to limitations of the techniques, equipment and experimental errors during the analysis.

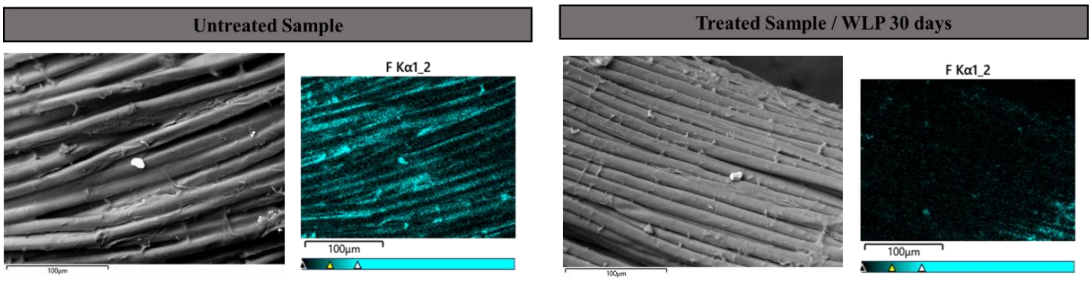


Figure 48 Compositional maps for fluorine for the untreated sample and for the treated sample with WLP 0% H_2O_2 for 30 days.

The compositional maps for F were obtained in several points of each sample. In Figure 48, for the untreated sample, there is a higher density of fluorine, indicating the presence of the protective PTFE coating layer. After the treatment using WLP for 30 days there is a reduction in fluorine distribution, with a reduction in its density. This indicates the partial removal of PTFE coating in the outer shell samples, corroborating the fact that polyamides remain intact after treatment with white lamp photolysis. This PTFE coating layer removal is expected and occurs naturally with the use of the turnout[143]. All maps obtained are available in appendix. In view of the results, despite a reduction in the tearing resistance, it can be considered that decontamination with photolysis is a viable alternative in the removal of PAHs in PFPC, considering that washing the suits causes greater damage to the fibers.

4.8. <u>Fifth Step:</u> Three-Layer Fabrics Decontamination

In the last part of the experimental design, the WLP decon was compared with the traditional physical decontamination methods (simulated laundering and wet-soap brushing). For that, pieces of three-layer fabrics were contaminated with pyrene and 9-methylanthracene. The photolysis was carried out according to previous tests carried out with the outer layer and carried out with a 250 W white mixed lamp, model E27, Luz Sollar® for 3 days. This sample was used so that a more realistic experiment could be done. After performing the tests, the samples were extracted with acetonitrile and the extracts analyzed by UV/VIS for the quantification of PAHs. Degradation rates and spectra related to each decontamination are depicted in Figure 49.

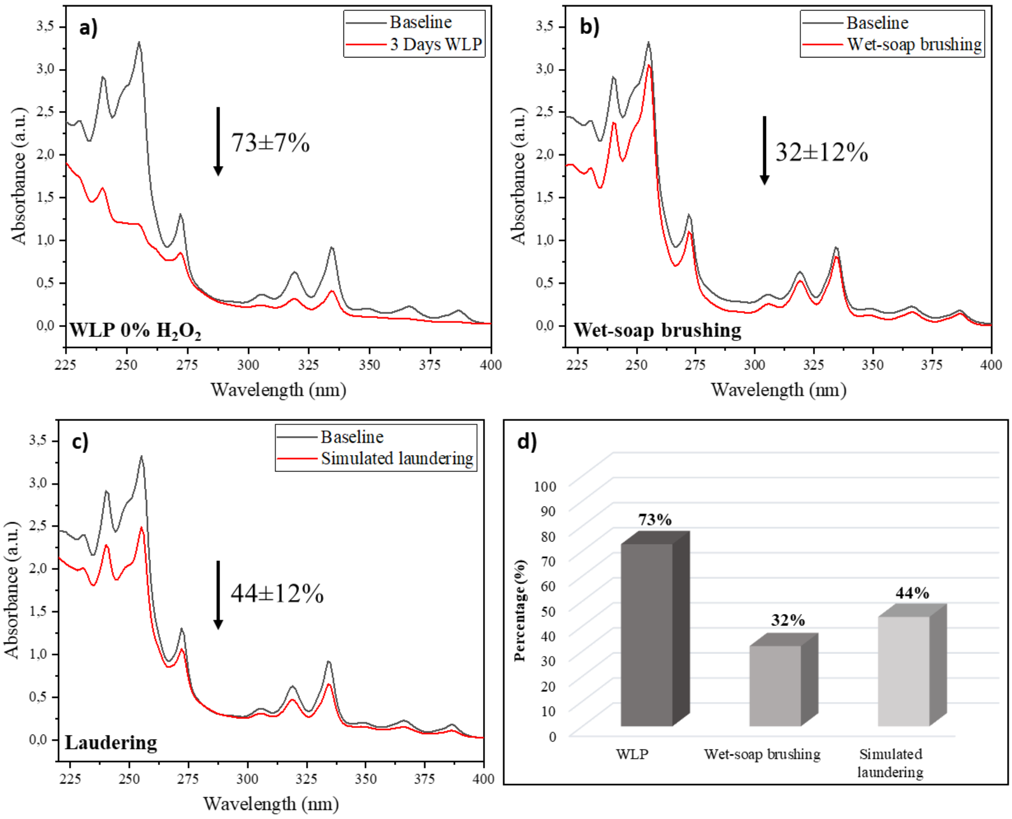


Figure 49. UV/VIS spectra of decontamination procedure performed **(a)** WLP decon for 3 days with 0% of H_2O_2, **(b)** simulated laundering decon, **(c)** wet-soap brushing decon and **(d)** PAH removal percentage.

The wet-soap brushing reduced it by 32±12% (Figure 49b) and the simulated laundering showed a reduction of 44±12% of PAHs (Figure 49c), while the decontamination via photolysis showed the best result, 73±7% (Figure 49a). This result suggests that photolysis with white lamp is efficient in removing the PAH and could be an alternative for cleaning suits. It is noteworthy that the results were obtained in samples of a smaller scale, especially in the washing machine experiment. The bucket adaptation does not promote the friction that facilitates washing, which is generated in the conventional washing machine. This may have lowered decontamination rate. Comparing to what is described in the literature, some authors describe more efficient results in physical decon methods in the removal of analytes than those described in this work. For instance, Fent *et al.*[64] showed 85% of PAH contamination by wet-soap decon. On the other hand, Banks *et al.*[97] showed the laundering did not promoted the total removal of the PAHs and other compound deposited after the firefight. In fact, in some cases, they found a higher concentration, indication a cross-contamination.

One of the main complaints related to laundering and wet-soap brushing is the fact that turnout gear can get wet after decontamination. This increases the risk of burns, in addition to the discomfort and weight carried by the firefighter[84]. The WLP decon allowed the removal of PAHs in a simple way, being a dry method, relatively fast, efficient, with good rates of reduction in PAH concentration. Another advantage of WLP decon is that there is a lower risk of cross contamination. The firefighter ends up having less contact with the contaminated protective clothing. In Brazil, laundering is mostly done at home [144], what increase the risk of contaminating other pieces of clothes or even other residents due to the contamination of the washing machine. With photolysis, this cross contamination tends to be reduced since WLP stations can be easily installed in the corporation itself. Moreover, WLP photolysis is a more ecofriendly than laundering, because it avoid removed compounds are dumped into the sewage system.

Other important fact is the durability of the turnout gear. The washing process can promote further fiber degradation. Horn *et al.*[76] identified a reduction in tearing strength tests after laundering. The group evaluated the three layers of fabric and three methods of decontamination: laundering in a washing machine, wet-soap brushing and dry brushing. Laundering had lower trap tear strength than the other treatments evaluated. After 10 washes, there was a reduction of 1.2% - 9.1%. With 20 washes, the reduction was 9.3% - 19.6% and with 40 washes it was 24.1% - 41.1%. Fabrics that were machine laundering, tear strength dropped below 100 N, minimum requirement following NFPA 1971[142].

5. Conclusion and Perspectives

The goal of this work was to investigate the effectiveness of a chemical method of decontamination of proximity firefighting protective clothing for degradation of polycyclic aromatic hydrocarbons based on photolysis. The method would be an alternative to the physical decon processes already used by firefighters.

The use of UV (ULP) and white (WLP) lamp, as well as H_2O_2 and temperature, were investigated. The WLP promoted the removal of pyrene and 9-methylanthracene analytes deposited on fabrics of the outer layer of firefighter turnout, without the need to add an oxidizing agent. After 3 days, the method promoted the removal of 81±8% of both PAH following a pseudo-second-order rate. Mass spectra were obtained, and 3,4-dihydro-4-phenyl-2H-1-Benzopyran-2-one (RT 21.529 min), 9,10-Anthracenedione(RT 23.593 min), Methyl 2-benzoylbenzoate (RT 24.133 min) and 1a,9b-dihydro- 1H-Cyclopropa[l]phenanthrene (RT 24.224 min) were identified as by-products. All by-products formed during the reaction also underwent photolysis reaction and their concentration decreased after 3 days.

The proposed decontamination technique was compared with the commonly applied techniques, laundering and wet-soap brushing, on three-layer fabrics. Photolysis showed a removal of 73±7% of the deposited PAHs, while simulated laundering removed 44±12% and wet-soap brushing 32±12%.

Regarding the fabric analysis, the protective clothing outer shell fabrics submitted to photolysis (without the PAH) was evaluated to assess whether the photolysis decon promoted the deterioration of the fibers. The chemical structure of the fibers was evaluated by FTIR/RTA and no important changes was observed. The tearing strength test presented a reduction of 17% - 26% after 30 days of WLP with 0% of H_2O_2. This reduction is not necessarily due to fiber degradation but can be related to removal of fabric's water repellant coating, evidenced by decrease of fluorine in SEM/EDS maps. Also, no changes were observed in the fibers´ morphology.

In view of these results, the 3 days WLP without H_2O_2 is an efficient decon method for the removal of PAH deposited in the proximity firefighting protective clothing, maintaining fabric´s integrity and properties.

The WLP decon has several advantages in comparison to what is currently performed. Besides promoting greater removal of PAHs than the physical decon techniques, for the WLP it is not necessary to wet the turnout to decontaminate it, which can result in burns if the suit is used wet. Also, physical decon can promotes a greater loss of physical and thermal protection properties of the fabrics. In addition, the technique developed is simple, cheap, and environmentally friendly and safer for the firefighter, as it reduces his contact with contaminants.

There is still a long way to go, and other tests must be carried out. Other lamps must be tested, both with emission in the UV region, as well as in the visible area of the spectrum. Regarding the use of the oxidizing agent, one option would be to use a higher concentration, in addition to the use of water vapor, which could improve the photolysis reaction. Finally, it is important to evaluate the photolysis reaction of other compounds, PAHs and other contaminants, deposited on firefighters' suits.

6. Appendix

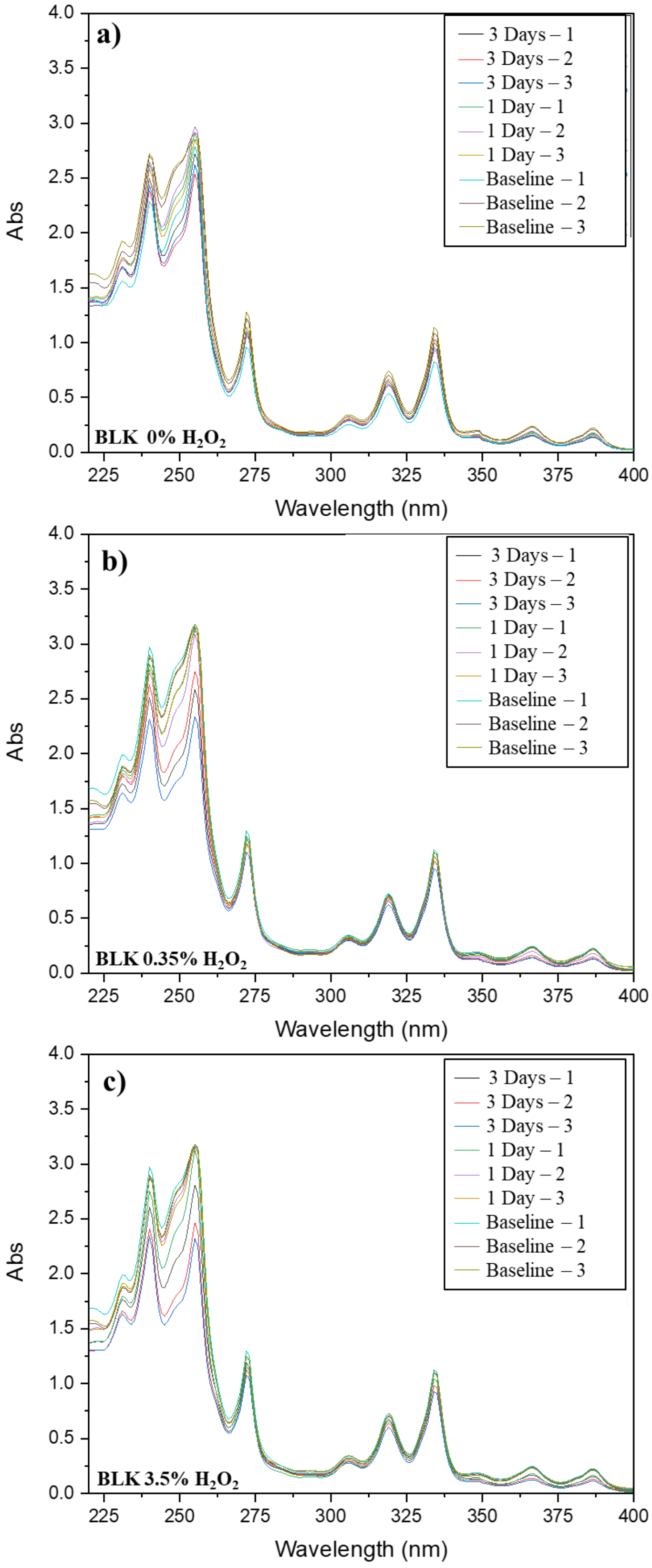


Figure S20. UV/VIS spectra of experiments performed in 1 and 3 days with **a)** BLK 0% of H_2O_2, **b)** BLK 0.35% of H_2O_2 and **c)** BLK 3.5% of H_2O_2

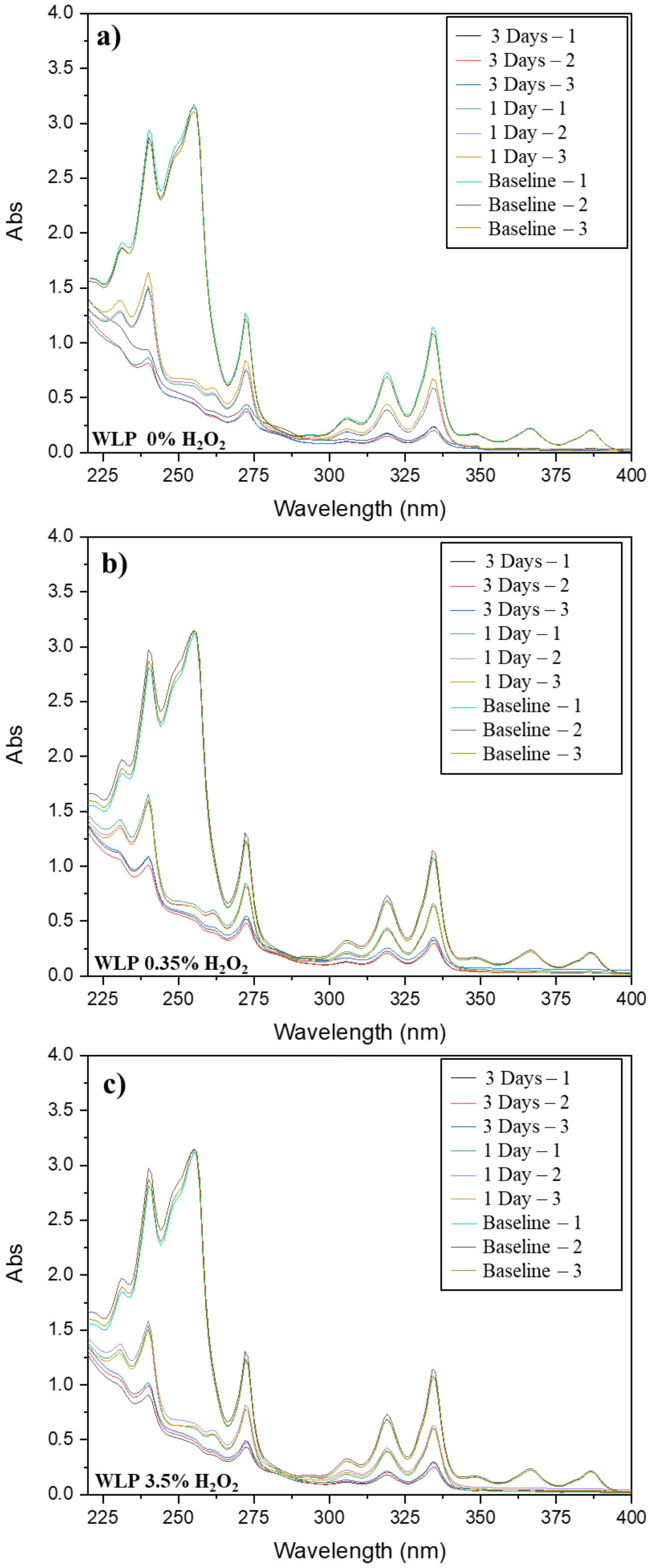


Figure S21. UV/VIS spectra of experiments performed in 1 and 3 days with **a)** WLP 0% of H_2O_2, **b)** WLP 0.35% of H_2O_2 and **c)** WLP 3.5% of H_2O_2.

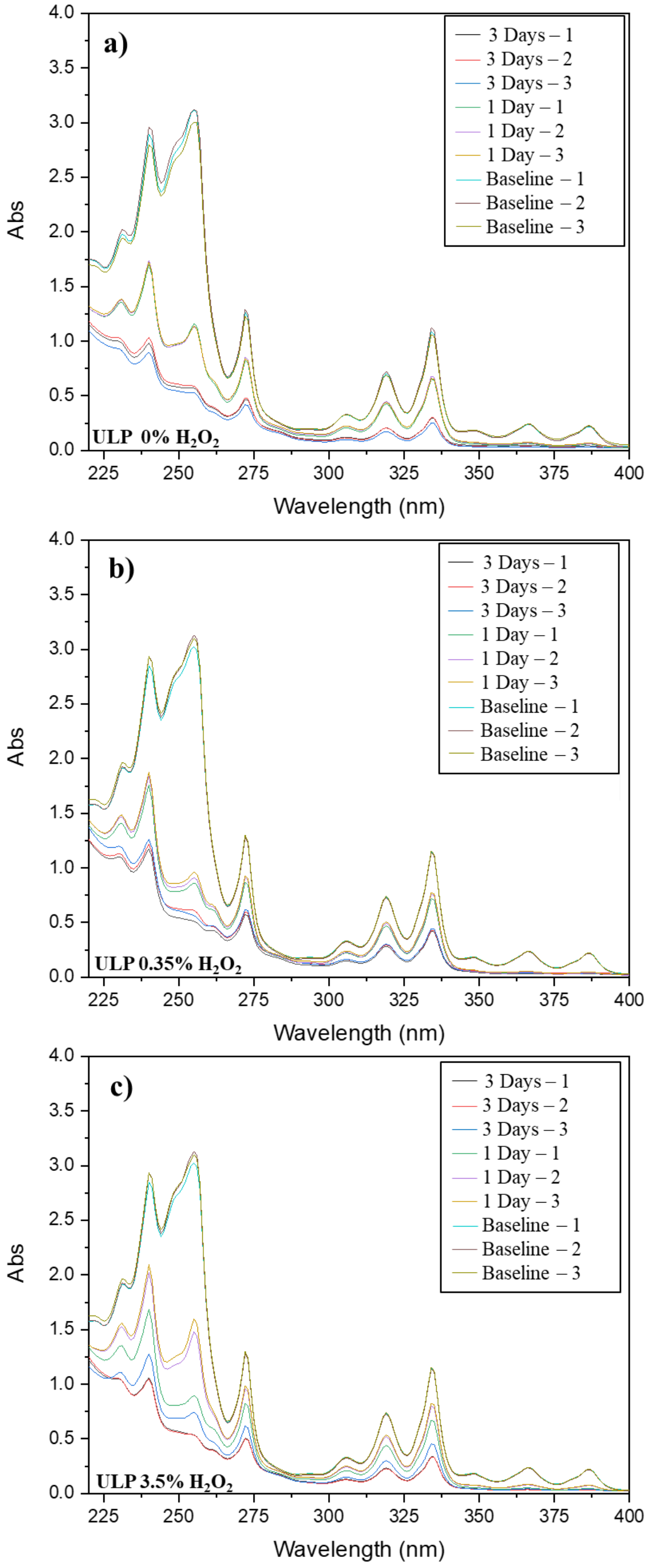


Figure S22. UV/VIS spectra of experiments performed in 1 and 3 days with **a)** ULP 0% of H_2O_2, **b)** ULP 0.35% of H_2O_2 and **c)** WLP 3.5% of H_2O_2.

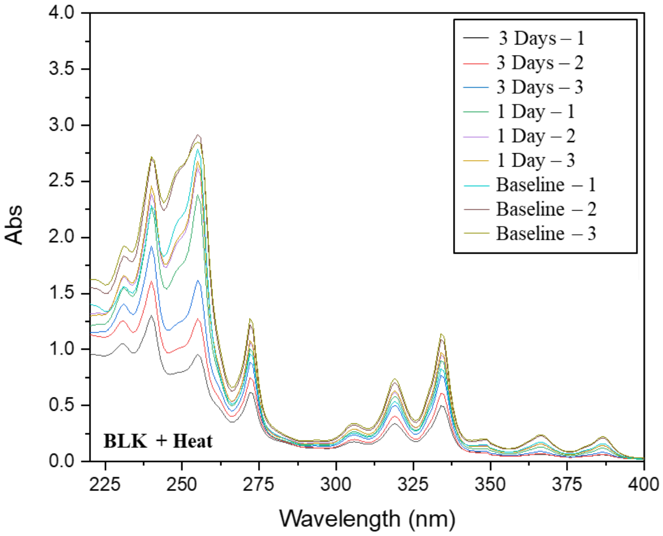


Figure S23. UV/VIS spectra of experiments performed in 1 and 3 days with BLK + heat 0% H_2O_2.

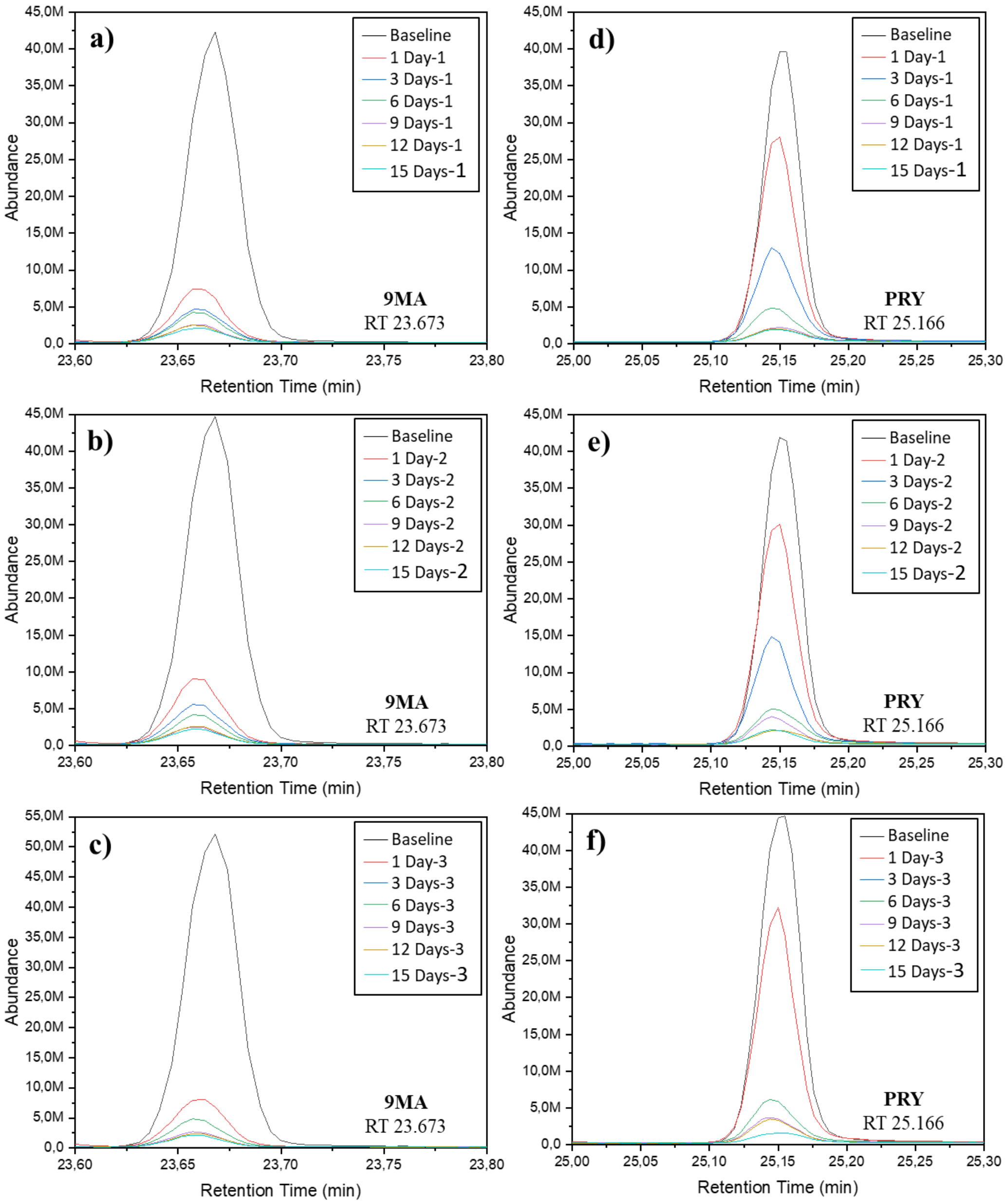


Figure S24. Chromatograms replicas of WLP 0% H_2O_2 experiments for the analyte 9-methylanthracene **(a-c)** obtained in the retention time of 23.673 min and for the analyte pyrene **(d-f)** obtained in the retention time of 25.166 min.

3,4-dihydro-4-phenyl-2H-1-Benzopyran-2-one
RT 21.529 min

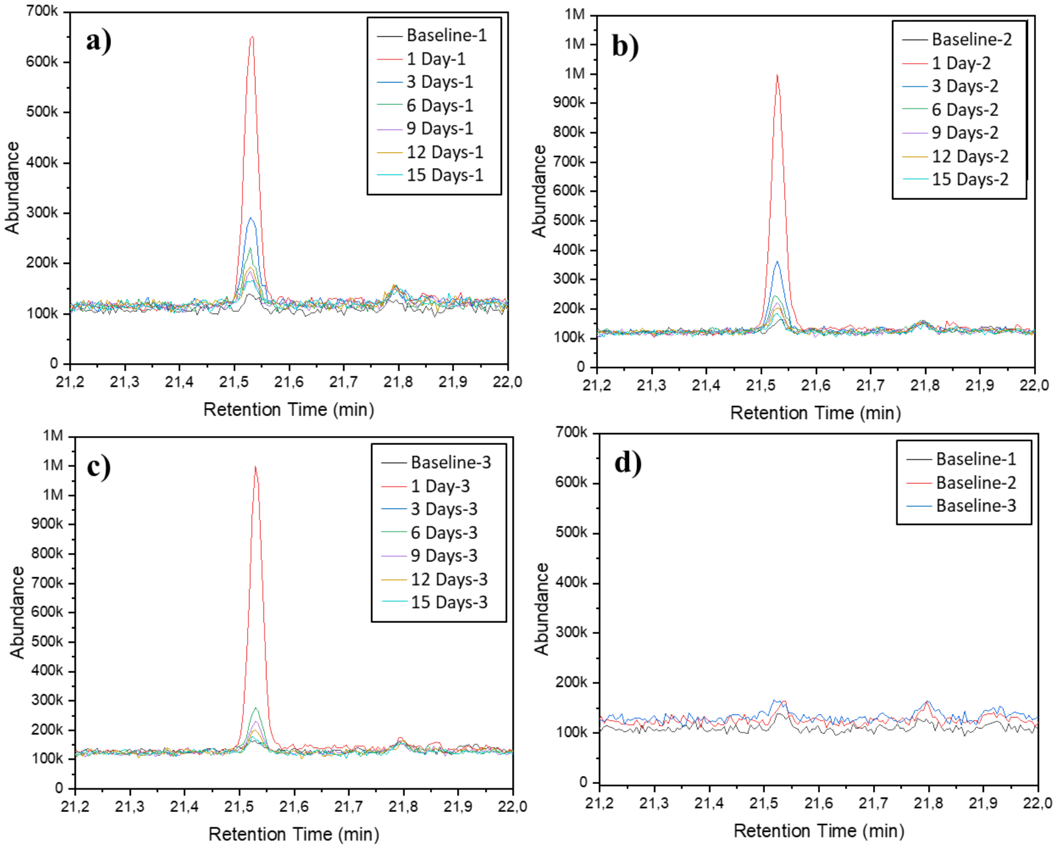


Figure S25. Chromatograms replicas **(a-c)** of WLP 0% H_2O_2 by-product 3,4-dihydro-4-phenyl-2H-1-Benzopyran-2-one obtained in the retention time of 21.529 min and **d)** chromatograms from the virgin fabric (baseline).

9,10-Anthracenedione
RT 23.593 min

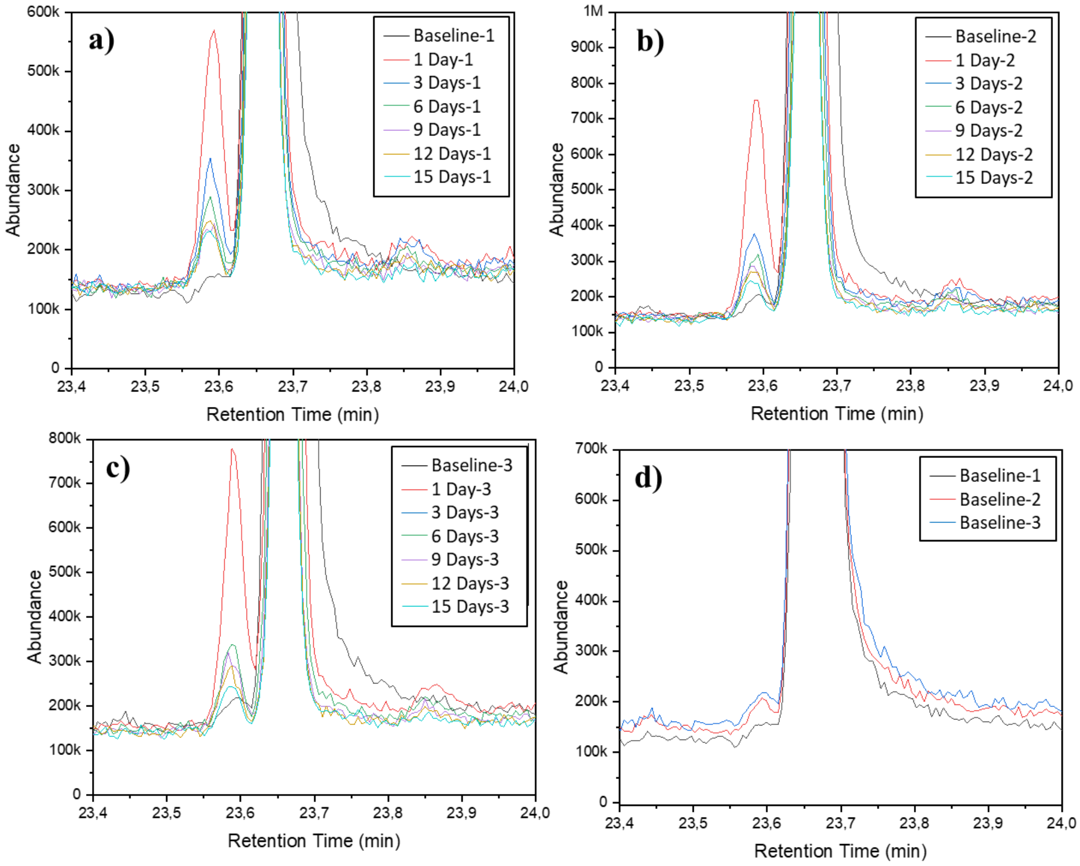


Figure S26. Chromatograms replicas **(a-c)** of WLP 0% H_2O_2 by-product 9,10-Anthracenedione obtained in the retention time of 23.593 min and **d)** chromatograms from the virgin fabric (baseline).

Methyl 2-benzoylbenzoate
RT 24.133
1a,9b-dihydro- 1H-Cyclopropa[l]phenanthrene
RT 24.224 min

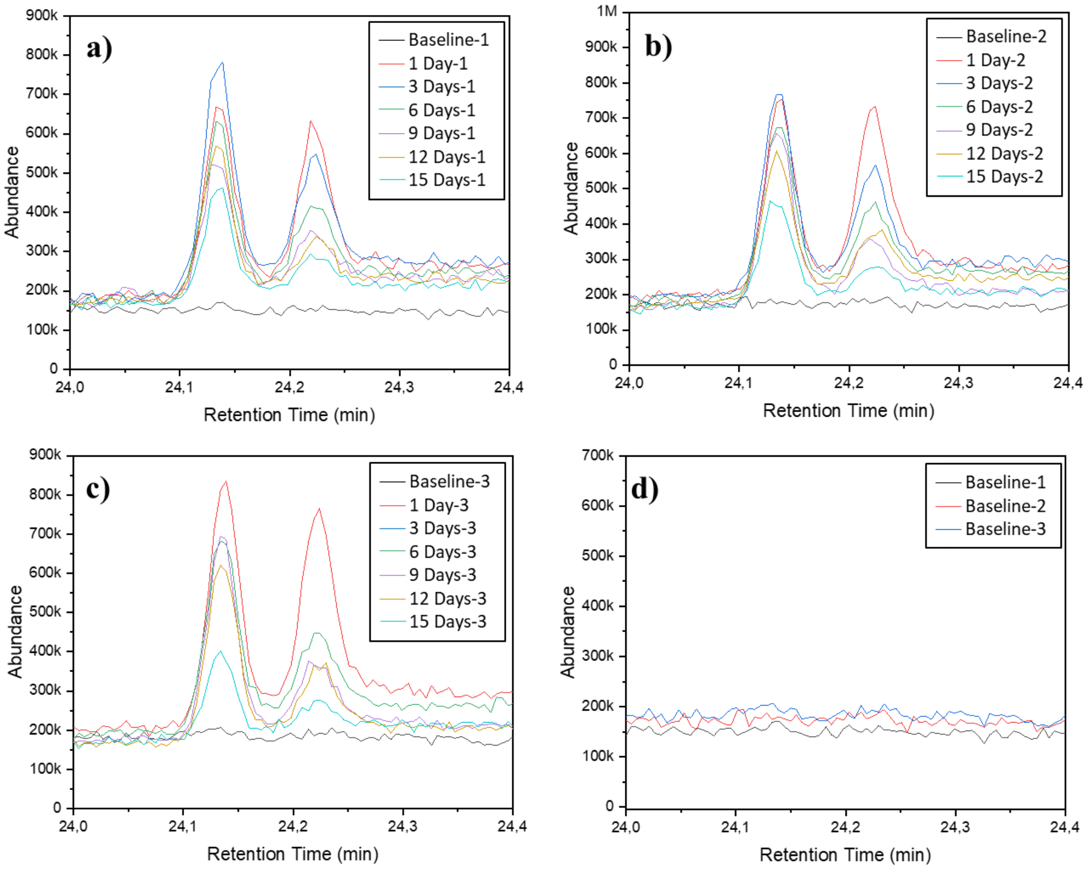


Figure S27. Chromatograms replicas **(a-c)** of WLP 0% H_2O_2 by-products Methyl 2-benzoylbenzoate and 1a,9b-dihydro- 1H-Cyclopropa[l]phenanthrene obtained in the retention time of 24.133 and 24.224 min and **d)** chromatograms from the virgin fabric (baseline).

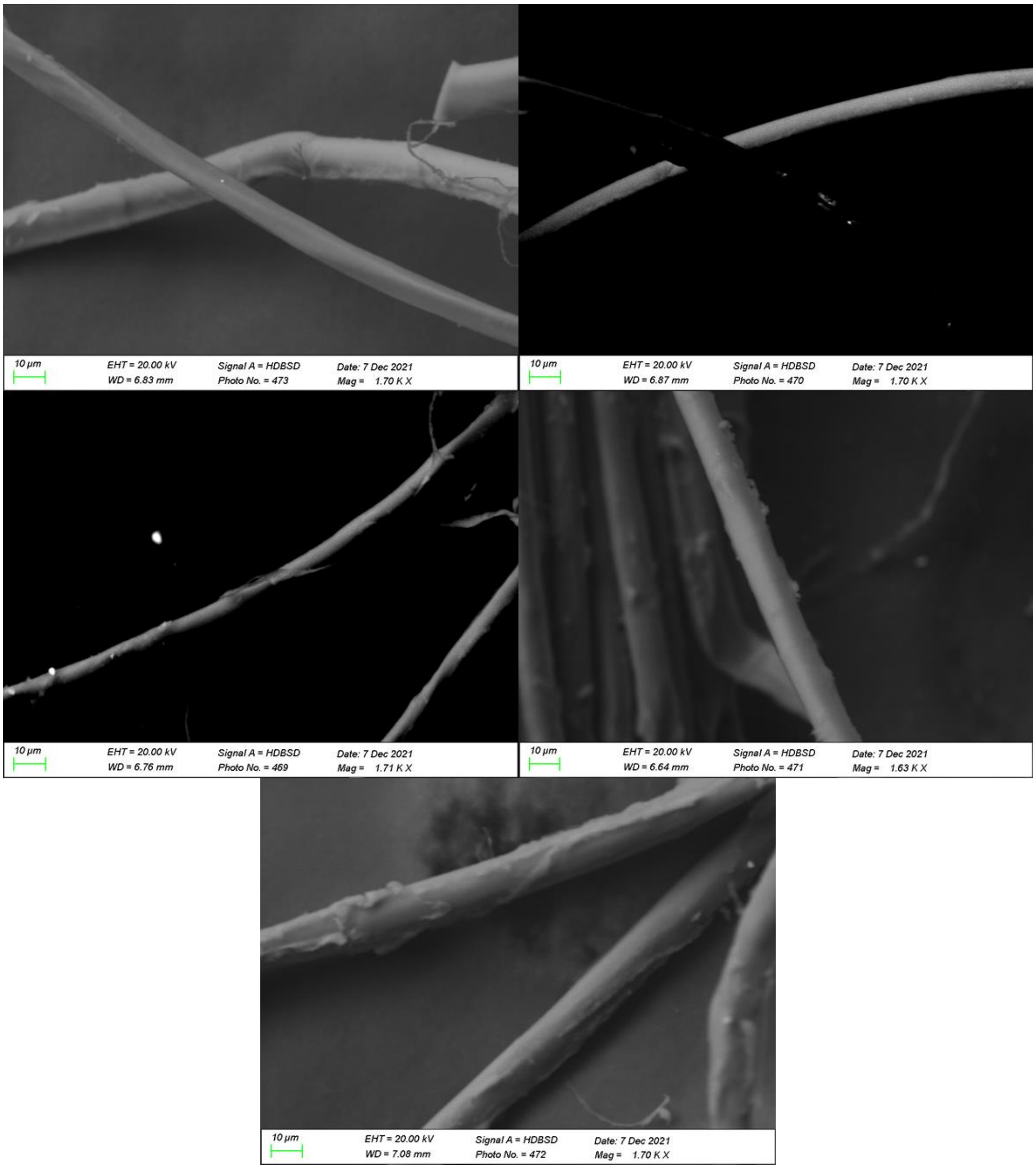


Figure S28. Micrographs of fibers before treatment.

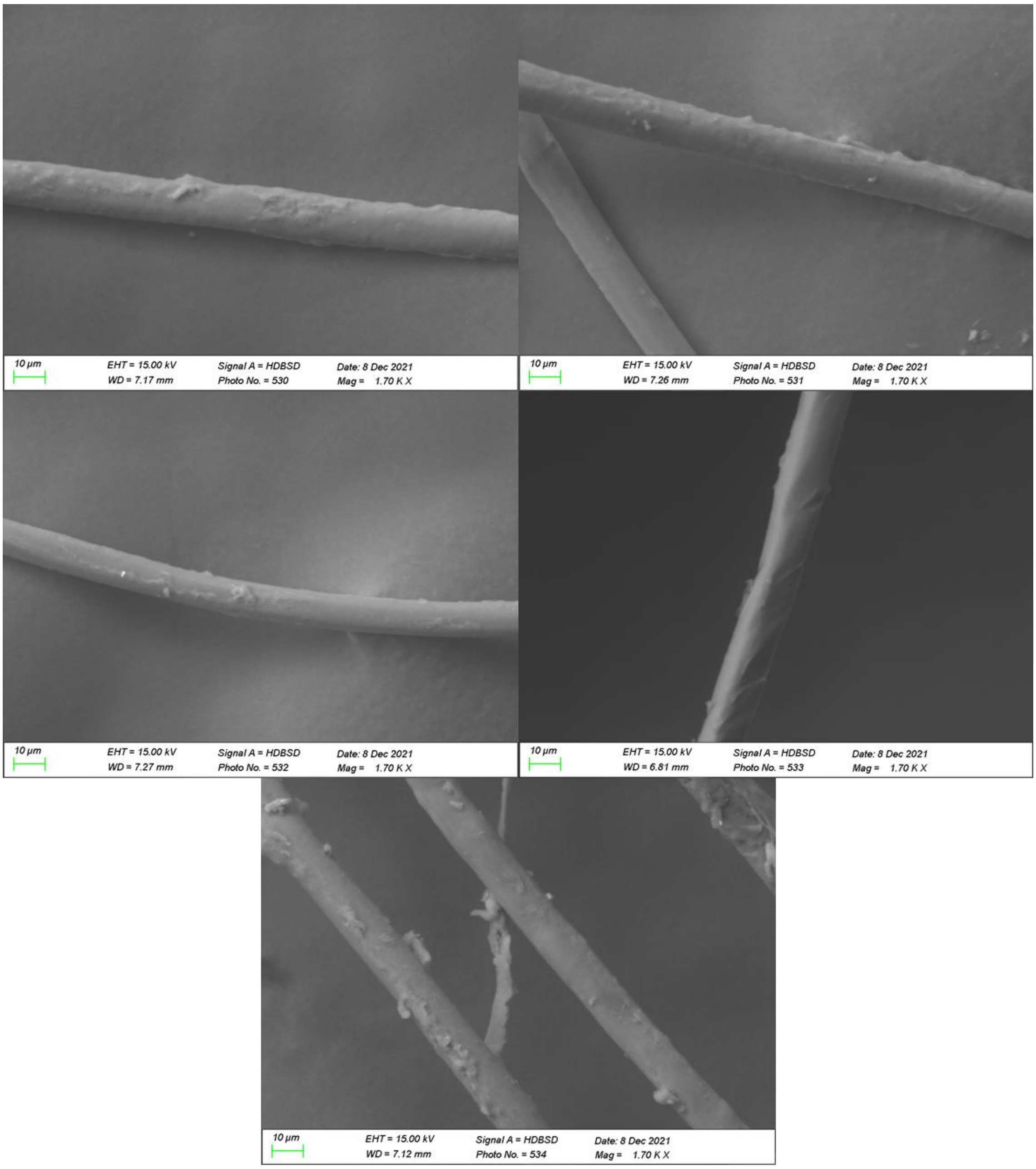


Figure S29. Micrographs of fibers after 3 days treatment with BLK 0% of H_2O_2.

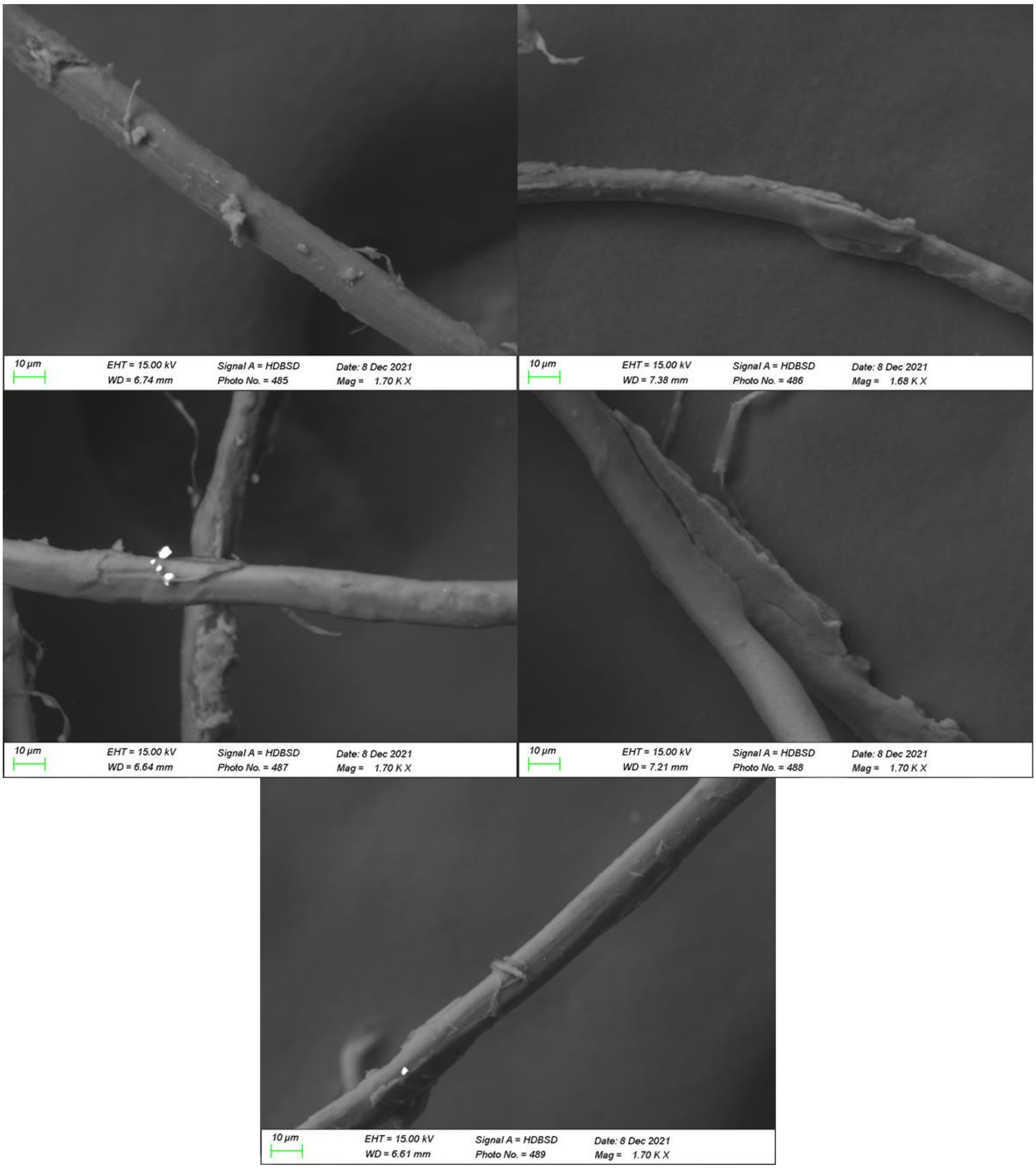


Figure S30. Micrographs of fibers after 3 days treatment with BLK 0.35% of H_2O_2.

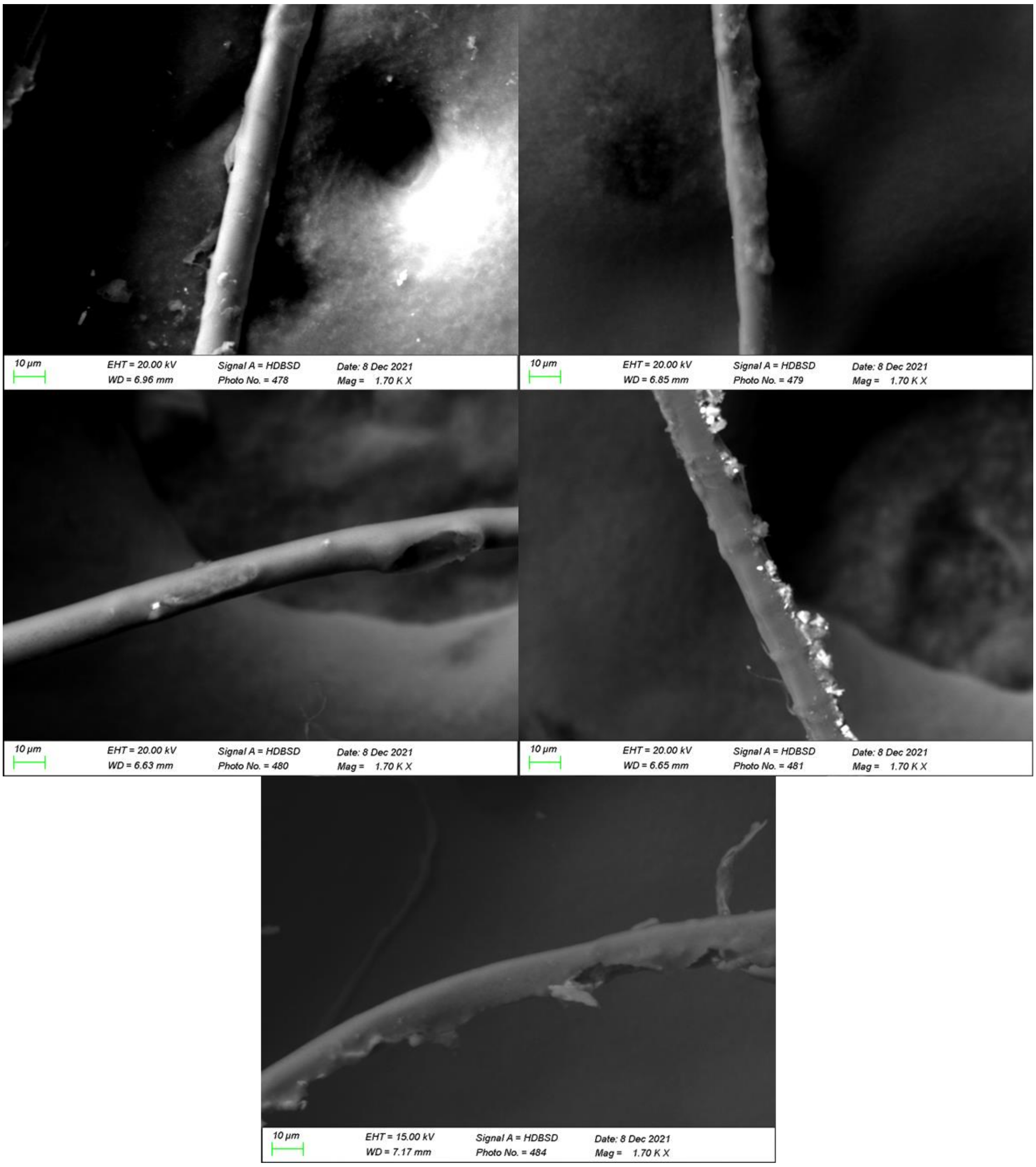


Figure S31. Micrographs of fibers after 3 days treatment with BLK 3.5% of H_2O_2.

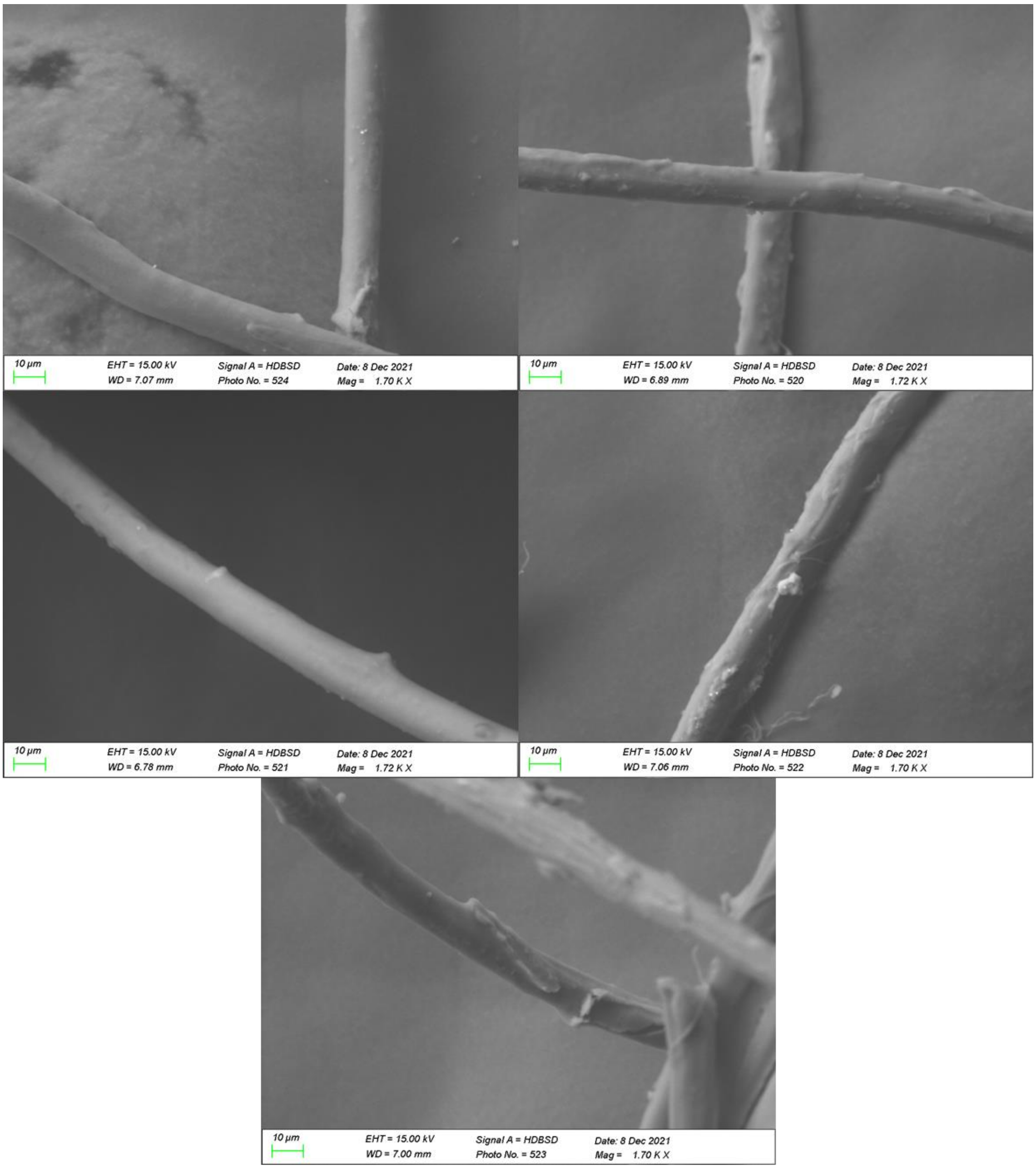


Figure S32. Micrographs of fibers after 3 days treatment with WLP 0% of H_2O_2.

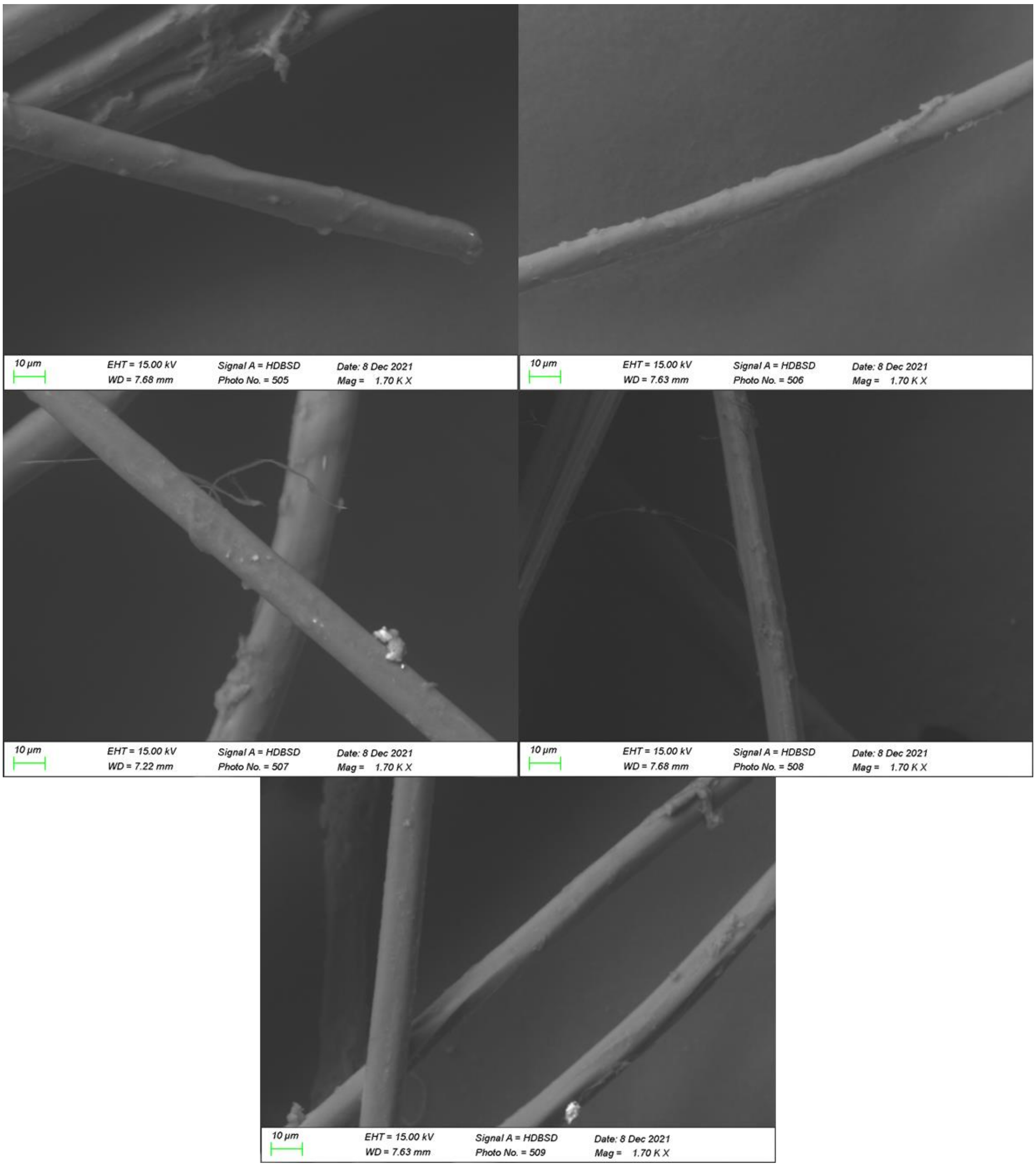


Figure S33. Micrographs of fibers after treatment WLP 0% of H_2O_2 for 30 days.

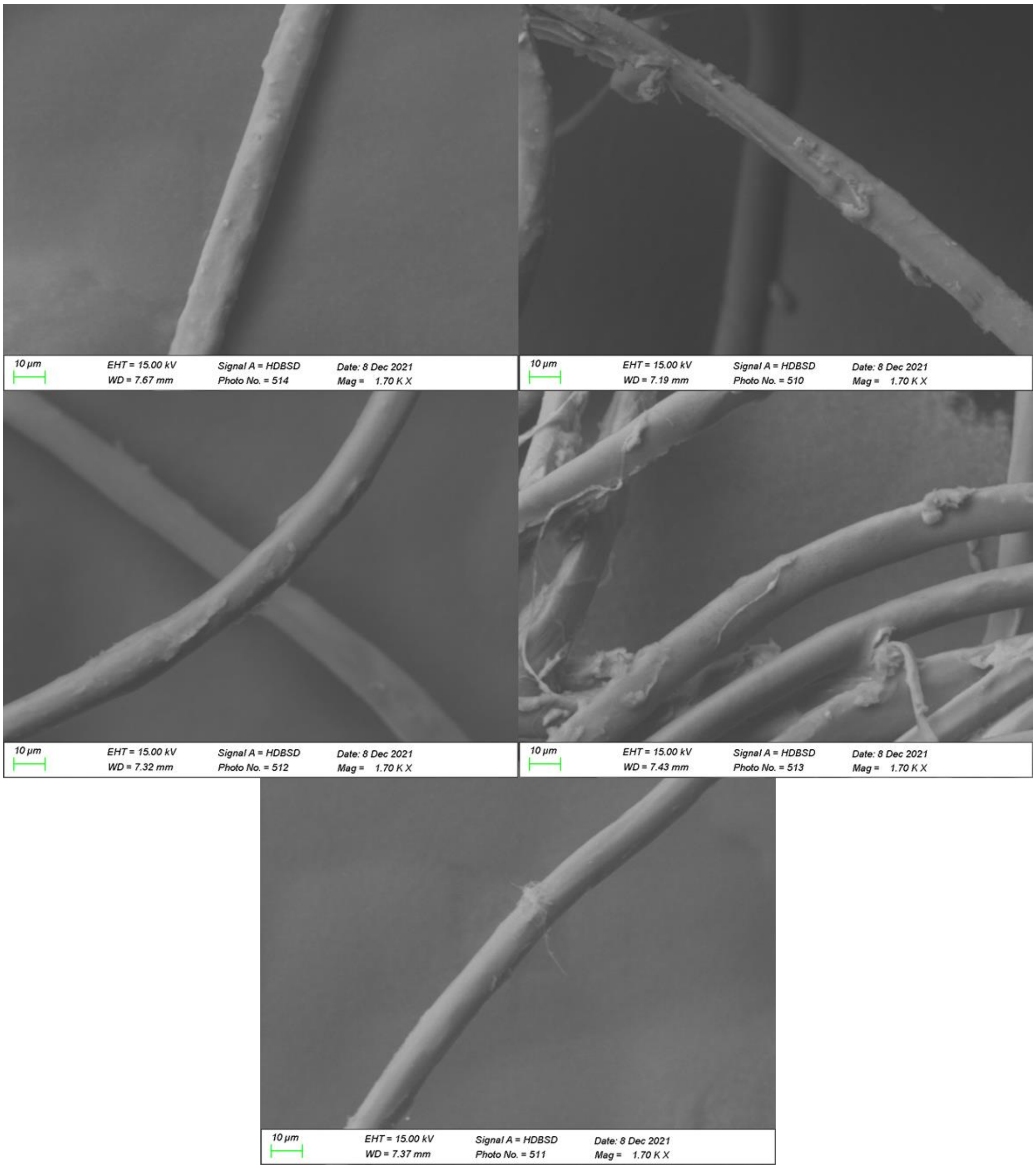


Figure S34. Micrographs of fibers after 3 days treatment with WLP 0.35% of H_2O_2.

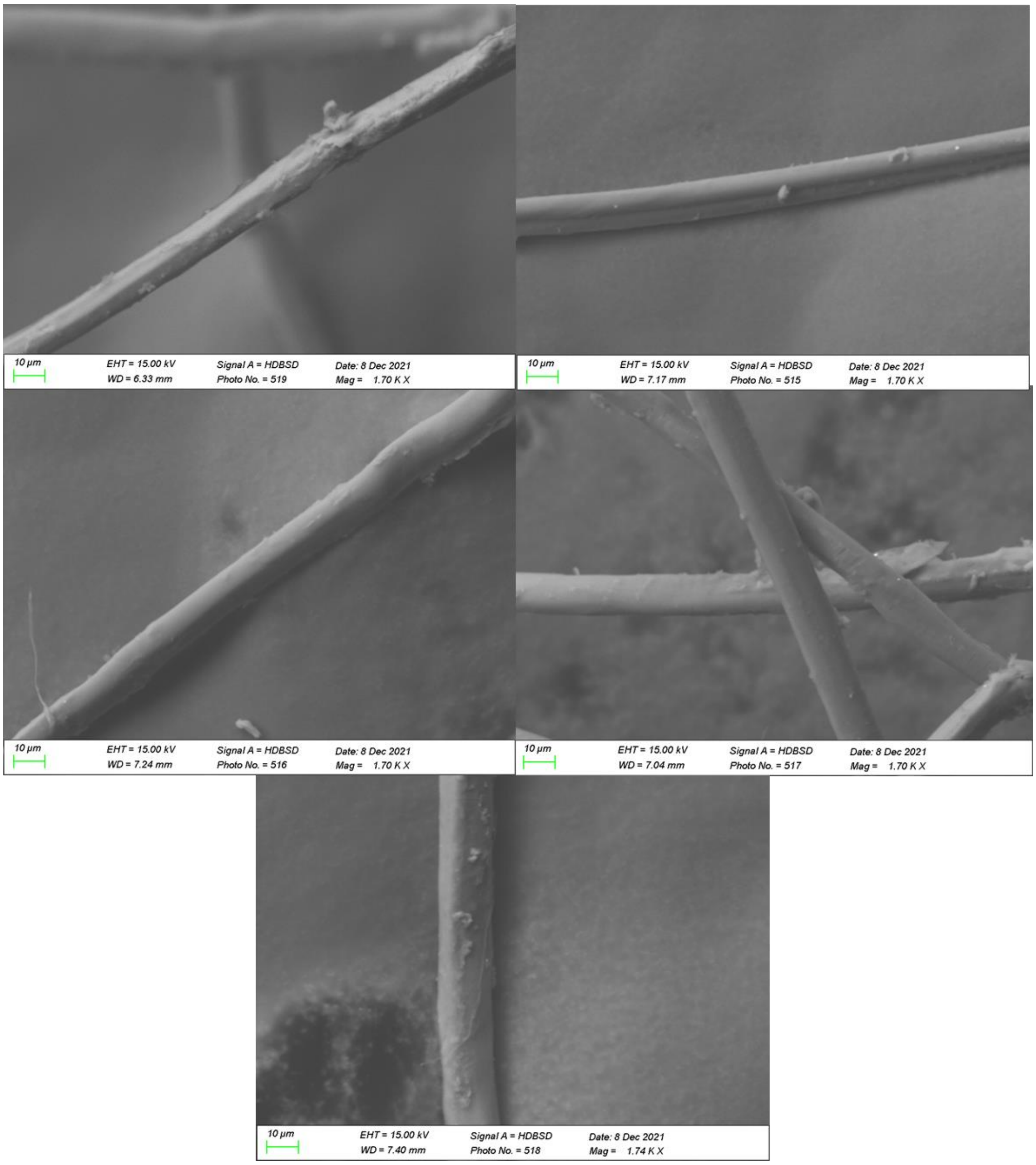


Figure S35. Micrographs of fibers after 3 days treatment with WLP 3.5% of H_2O_2.

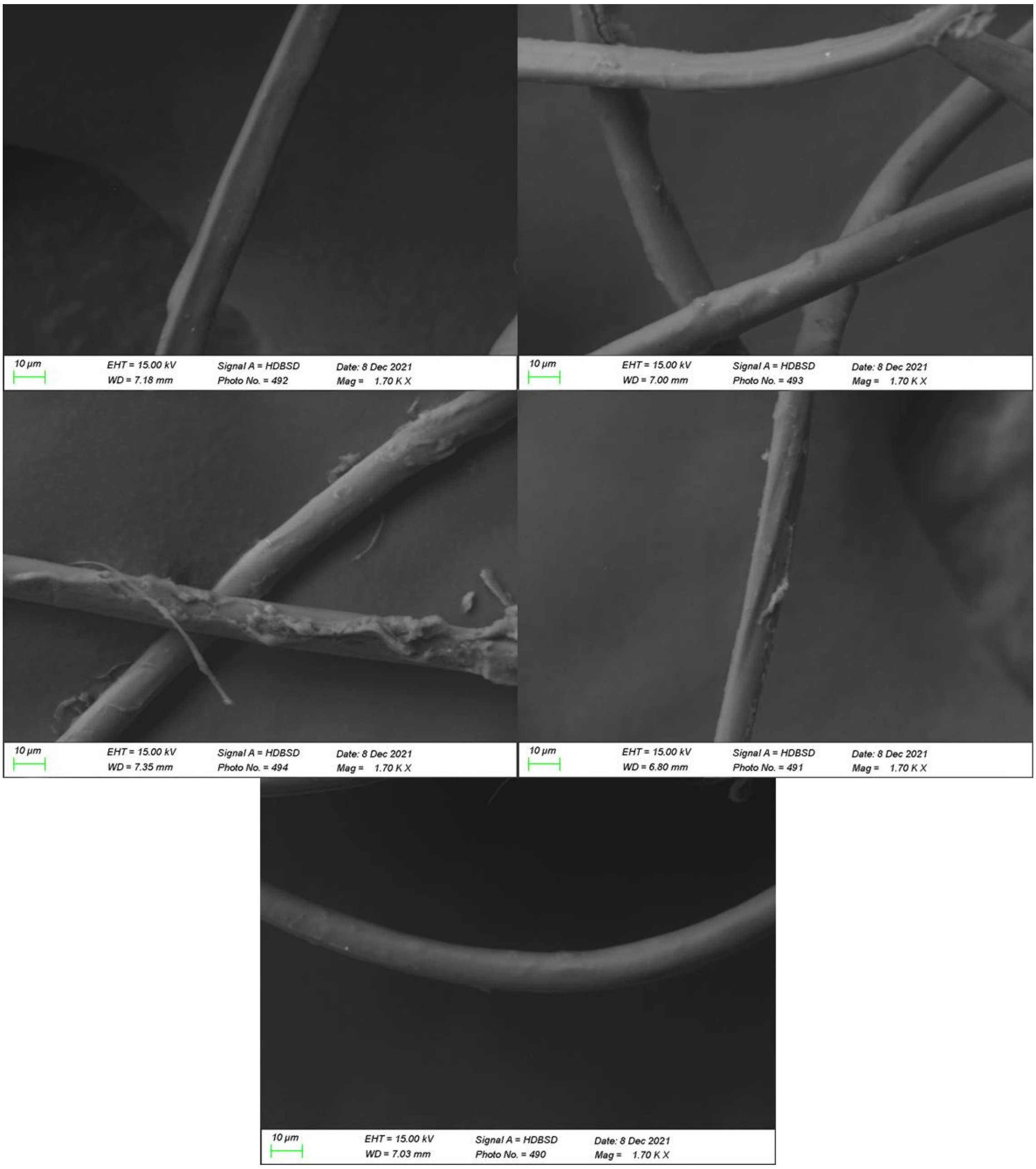


Figure S36. Micrographs of fibers after 3 days treatment with ULP 0% of H_2O_2.

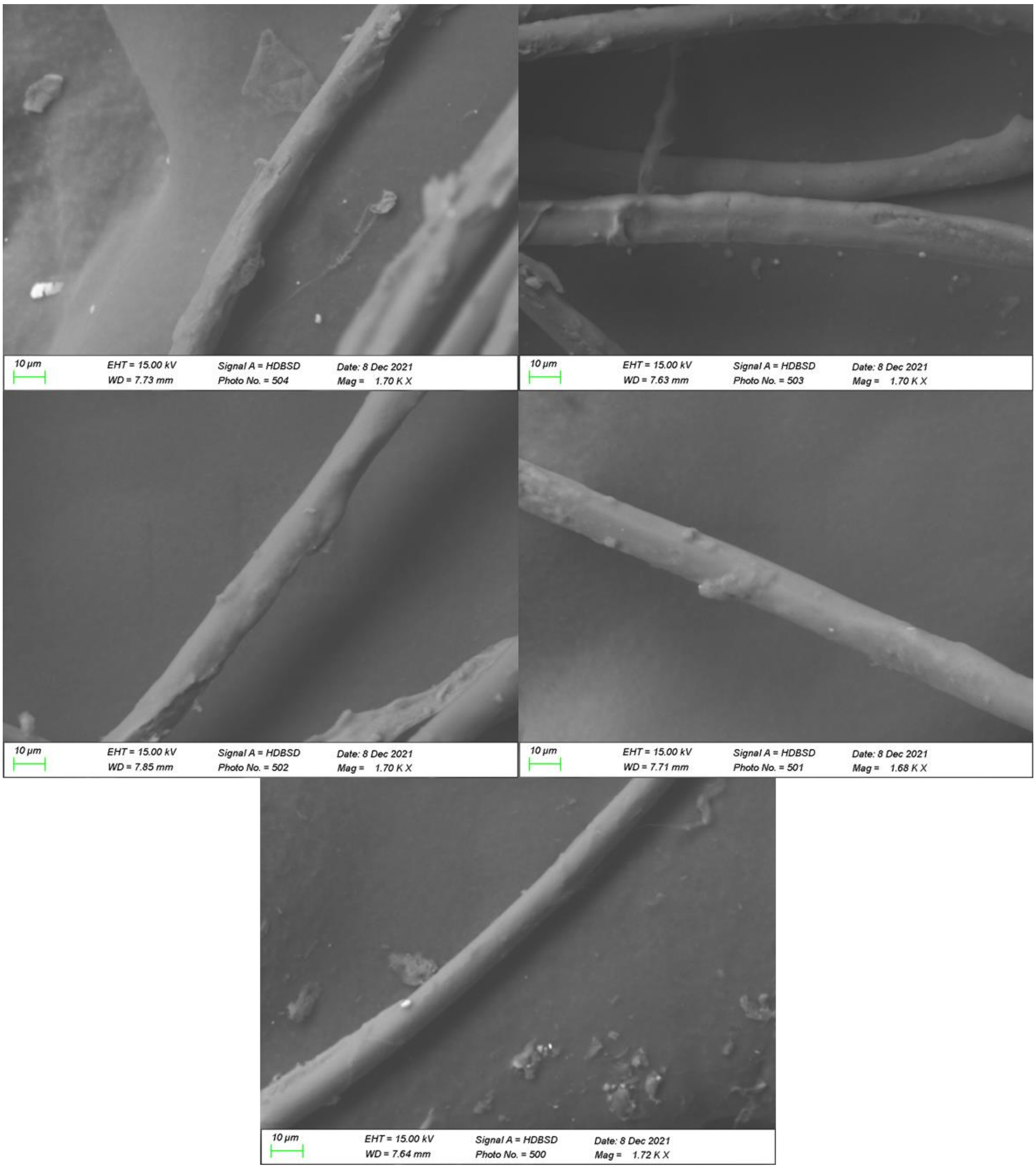


Figure S37. Micrographs of fibers after 3 days treatment with ULP 0.35% of H_2O_2.

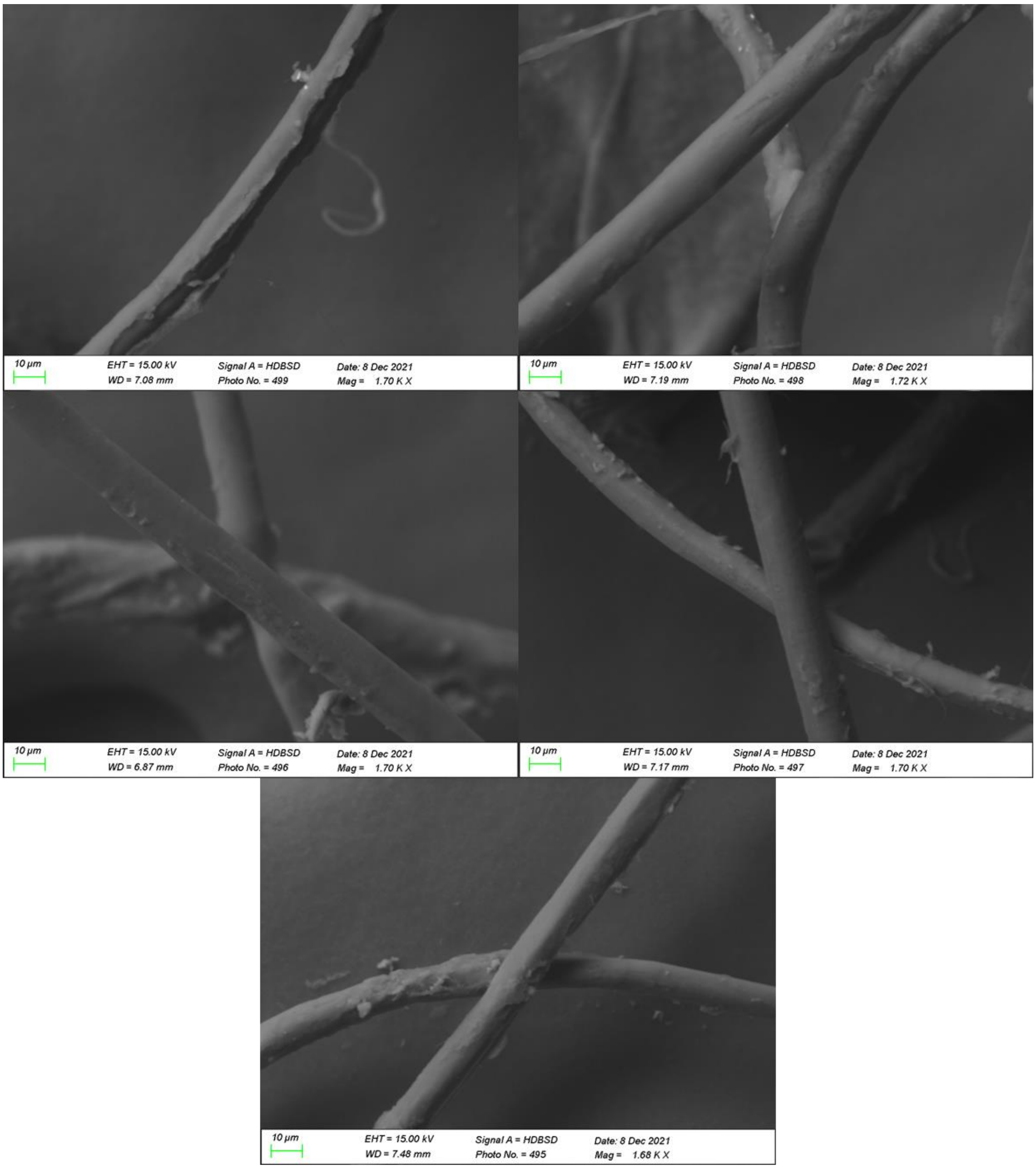


Figure S38. Micrographs of fibers after 3 days treatment with ULP 3.5% of H_2O_2.

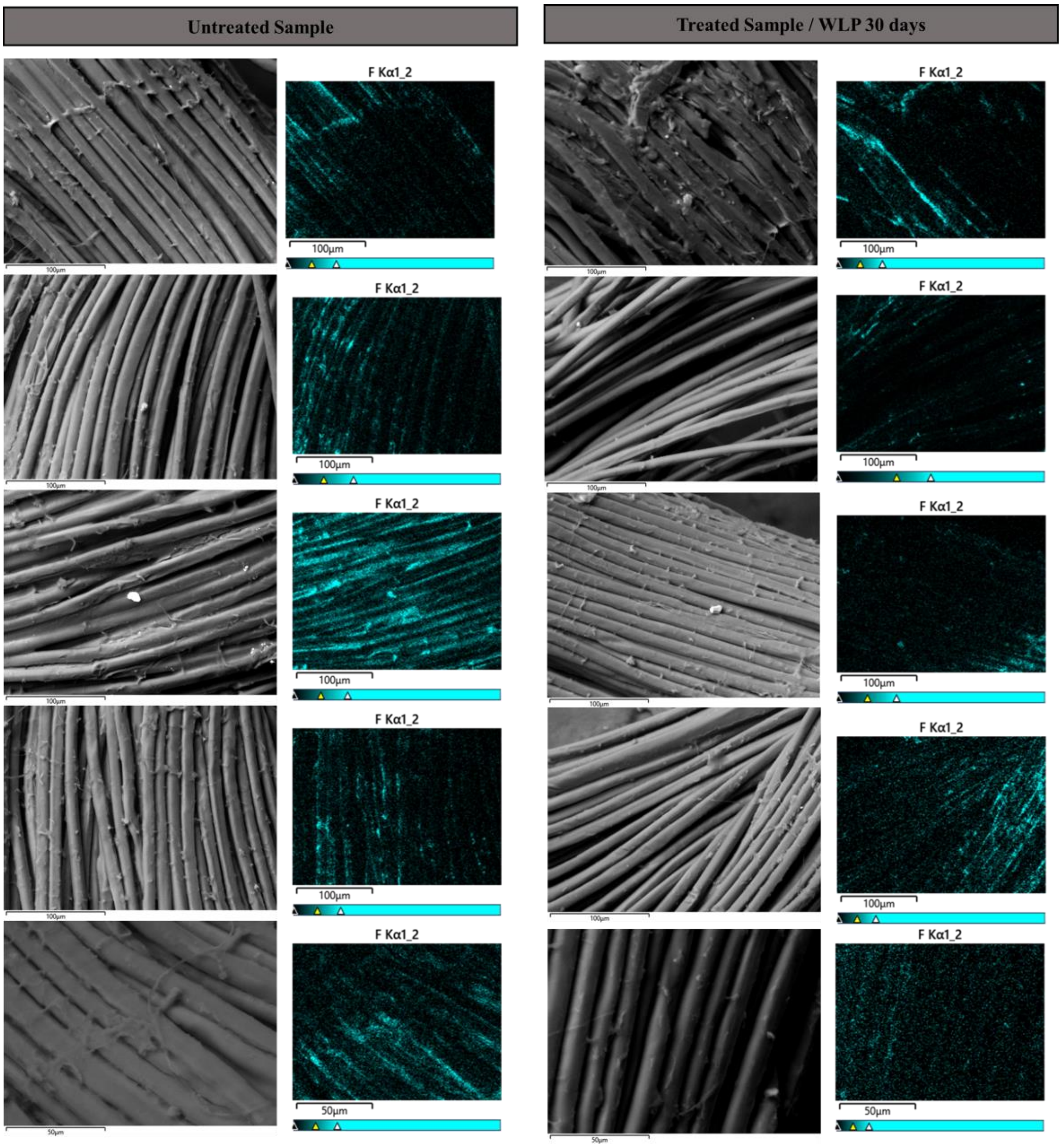


Figure S39. Compositional maps for fluorine for the untreated sample and for the treated sample with WLP 0% H_2O_2 for 30 days.

Table S26. Parameters of the chromatographic runs of the standard solutions.

Sample	***Retention Time***	***Area***	***Peak Width***	***Resolution***	***Tailing***	***PtP S/N***	***RMS S/N***	***No. of Theoretical Plates***
SS 1-1	23.68	1911513432	0.036	300.29	0.86	0.99	24.93	2336212
	28.17	1708480242	0.036	3.25	0.86	0.84	21.17	2635928
SS 1-2	23.68	1897767636	0.036	0	0.85	0.99	25.18	2379661
	25.17	1705028477	0.039	3.19	0.86	0.83	21.15	2256324
SS 1-3	23.68	1858731496	0.036	0	0.89	0.99	24.94	2390360
	25.16	1661443237	0.039	3.2	0.9	0.85	21.46	2362619
SS 2-1	23.68	1538866951	0.033	0	0.85	1.01	26.08	2795413
	26.16	1368948438	0.037	3.22	0.9	0.82	21.21	2505199
SS 2-2	23.68	1448019125	0.033	0	0.91	0.99	26.12	2913217
	25.16	1332971973	0.037	25	0.92	0.81	21.41	2507293
SS 2-3	23.68	1636487331	0.034	0	0.086	1	26.05	2702712
	25.16	1470212101	0.039	3.13	0.88	0.8	20.91	2329875

SS 3-1	*23.67*	*1115716087*	*0.03*	*0*	*0.94*	*1*	*26.52*	*3499841*
	25.16	1051277398	0.035	21.21	0.96	0.83	22.11	2934167
SS 3-2	23.67	1090079371	0.03	0	0.95	2	26.36	3484187
	25.16	1030473029	0.034	27.27	0.92	1	26.36	2960101
SS 3-3	23.67	1118712375	0.03	0	0.93	1	26.37	3404044
	25.16	1059328303	0.035	26.78	0.93	0.83	21.97	2827094
SS 4-1	23.67	658385027	0.028	0	1.07	0.98	25.42	3921418
	25.15	681361757	0.03	30.04	1.09	0.93	24.16	3860038
SS 4-2	23.67	654499964	0.028	0	1.06	0.99	25.92	4079360
	25.15	667949849	0.031	29.82	1.06	0.91	23.8	3612375
SS 4-3	23.67	599632957	0.027	0	1.12	1	25.41	4143836
	25.15	626123677	0.03	30.73	1.08	0.97	24.67	3987027
SS 5-1	23.67	255094710	0.26	337.72	1	0.98	20.76	4446229
	25.15	274693147	0.029	31.83	2	0.99	20.87	4283939

SS 5-2	*23.67*	*264664865*	*0.027*	*0*	*0.96*	*0.98*	*21.66*	*4320262*
	25.15	284098892	0.029	31.57	1.1	0.99	21.73	4264241
SS 5-3	23.67	262622653	0.027	0	0.98	0.96	21.88	4412813
	25.15	294368652	0.029	31.38	1.07	0.98	22.47	4077387
SS 6-1	23.66	33121384	0.028	0	1.04	0.76	4.52	3933715
	25.15	44556275	0.03	29.97	1.03	0.98	5.8	3799737
SS 6-2	23.66	31697111	0.029	0	1.06	0.72	4.4	3593211
	25.15	42072441	0.031	29.13	1.03	0.97	5.93	3697615
SS 6-3	23.66	32467745	0.03	0	1.03	0.62	4.27	3424360
	25.15	42155348	0.031	28.84	1.06	0.8	5.49	3737813

Table S27. Parameters of the chromatographic runs of the WLP 0% H_2O_2 experiments – 0 day.

Sample	*Retention Time*	*Area*	*Peak Width*	*Resolution*	*Tailing*	*PtP S/N*	*RMS S/N*	*No. of Theoretical Plates*
WLP 0% H_2O_2 0 Days - 1	23.67	745862172	0.029	89.61	1.05	0.88	19.85	3798991
	25.15	782088637	0.031	29.43	1.03	0.84	18.94	3659431
WLP 0% H_2O_2 0 Days - 2	23.67	801637901	0.029	89.68	0.96	0.90	19.78	3746280
	25.15	846698360	0.032	28.69	1.04	0.85	18.75	3363321
WLP 0% H_2O_2 0 Days - 3	23.67	952734007	0.029	89.71	0.95	0.96	20.35	3578655
	25.15	948754411	0.034	27.59	0.92	0.83	17.61	3020597

Table S28. Parameters of the chromatographic runs of the WLP 0% H_2O_2 experiments – 1 day.

Sample	*Retention Time*	*Area*	*Peak Width*	*Resolution*	*Tailing*	*PtP S/N*	*RMS S/N*	*No. of Theoretical Plates*
WLP 0% H_2O_2 1 Days - 1	23.66	130445587	0.028	44.42	1.02	0.14	3.99	3970653
	25.15	558301206	0.032	29.44	1.08	0.52	15.16	3490866
WLP 0% H_2O_2 1 Days - 2	23.66	161506658	0.028	1.39	0.94	0.18	5.10	4013419
	25.15	610894356	0.033	19.60	1.08	0.60	16.89	3314285
WLP 0% H_2O_2 1 Days - 3	23.66	146912552	0.029	1.47	1.00	0.15	4.28	3621625
	25.15	639779156	0.032	16.05	1.03	0.61	17.08	3458435

Table S29. Parameters of the chromatographic runs of the WLP 0% H_2O_2 experiments – 3 days.

Sample	*Retention Time*	*Area*	*Peak Width*	*Resolution*	*Tailing*	*PtP S/N*	*RMS S/N*	*No. of Theoretical Plates*
WLP 0% H_2O_2 3 Days - 1	23.66	84168479	0.029	113.66	1.03	0.09	2.85	3718090
	25.15	277945815	0.034	18.87	1.17	0.25	7.89	3001334
WLP 0% H_2O_2 3 Days - 2	23.66	100555261	0.029	113.87	1.05	0.10	3.22	3796429
	25.15	311972442	0.033	18.72	1.07	0.28	8.58	3184959
WLP 0% H_2O_2 3 Days - 3	23.66	104097475	0.029	112.12	1.06	0.11	3.36	3688006
	25.15	291432980	0.037	17.46	1.16	0.24	7.38	2624959

Table S30. Parameters of the chromatographic runs of the WLP 0% H_2O_2 experiments – 6 days.

Sample	*Retention Time*	*Area*	*Peak Width*	*Resolution*	*Tailing*	*PtP S/N*	*RMS S/N*	*No. of Theoretical Plates*
WLP 0% H_2O_2 6 Days - 1	23.66	74759654	0.028	115.46	1.03	0.09	2.89	3868325
	25.15	110107366	0.037	26.95	1.17	0.10	3.23	2596422
WLP 0% H_2O_2 6 Days - 2	23.66	71431289	0.028	115.45	1.05	0.07	2.16	4013391
	25.15	121775854	0.040	25.82	1.22	0.08	2.56	2173504
WLP 0% H_2O_2 6 Days - 3	23.66	84020883	0.028	115.14	1.08	0.09	2.74	3951283
	25.15	137773465	0.036	27.4	1.16	0.11	3.46	2103308

Table S31. Parameters of the chromatographic runs of the WLP 0% H_2O_2 experiments – 9 days.

Sample	*Retention Time*	*Area*	*Peak Width*	*Resolution*	*Tailing*	*PtP S/N*	*RMS S/N*	*No. of Theoretical Plates*
WLP 0% H_2O_2 9 Days - 1	23.66	46657517	0.030	112.17	1.04	0.050	1.67	3556133
	25.15	52873034	0.043	24.42	1.16	0.040	1.32	1940377
WLP 0% H_2O_2 9 Days - 2	23.66	43883743	0.028	115.04	1.09	0.05	1.62	3836256
	25.15	85562713	0.037	26.70	1.19	0.08	2.55	2522574
WLP 0% H_2O_2 9 Days - 3	23.66	47013957	0.030	111.65	1.08	0.05	1.55	3508196
	25.15	85848713	0.040	17.39	1.21	0.07	2.15	2226435

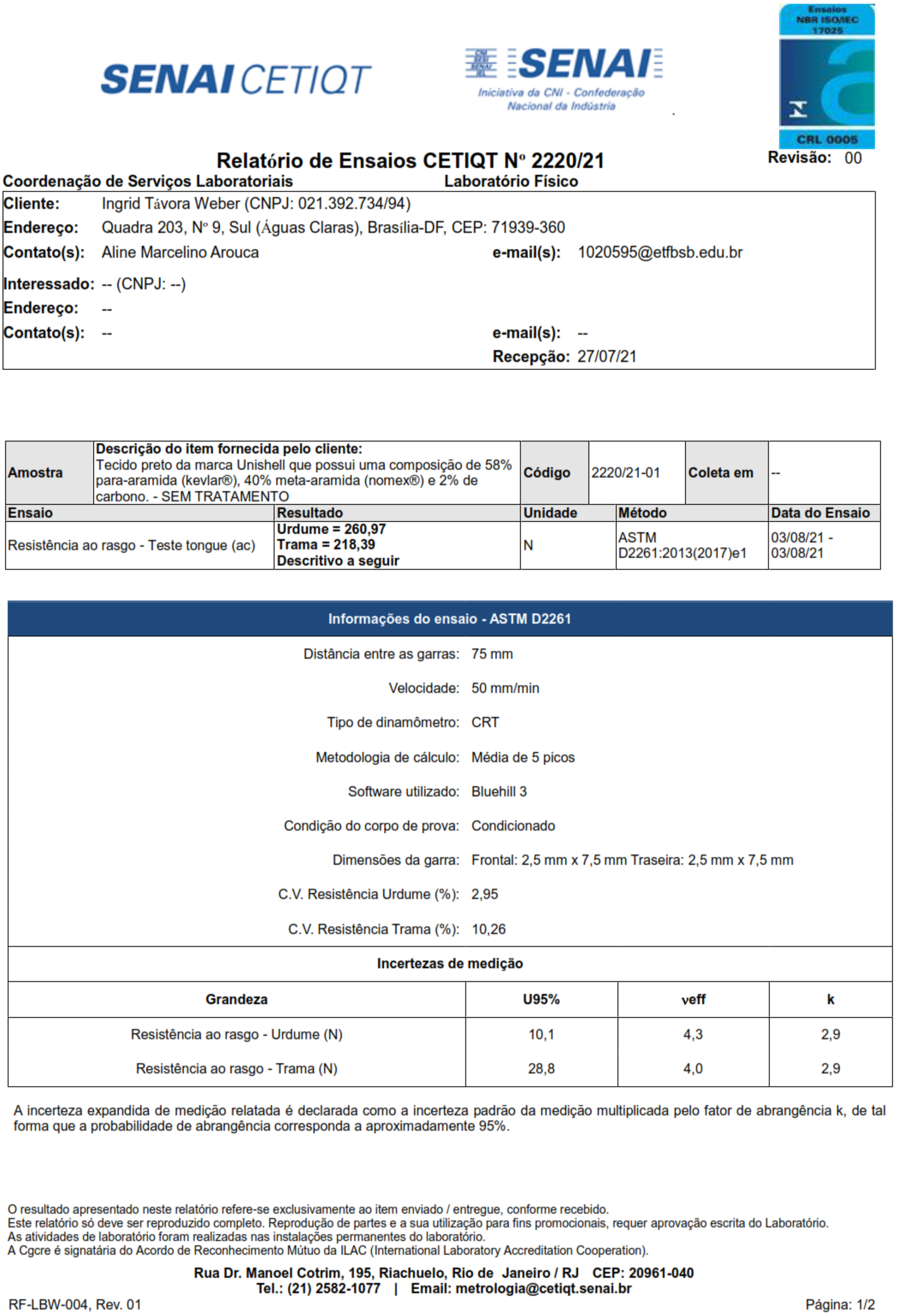
Table S32. Parameters of the chromatographic runs of the WLP 0% H_2O_2 experiments – 12 days.

Sample	*Retention Time*	*Area*	*Peak Width*	*Resolution*	*Tailing*	*PtP S/N*	*RMS S/N*	*No. of Theoretical Plates*
WLP 0% H_2O_2 12 Days - 1	23.66	44370019	0.029	114.37	1.08	0.04	1.44	3734918
	25.15	47237872	0.044	24.28	1.19	0.03	1.09	1850320
WLP 0% H_2O_2 12 Days - 2	23.66	45176342	0.029	111.47	1.06	0.01	1.45	3588355
	25.15	51826712	0.044	24.01	1.19	0.03	1.13	1822641
WLP 0% H_2O_2 12 Days - 3	23.66	45176342	0.029	111.47	1.06	0.04	1.45	3588355
	25.15	51826712	0.044	24.01	1.19	0.03	1.13	1822641

Table S33. Parameters of the chromatographic runs of the WLP 0% H_2O_2 experiments – 15 days.

Sample	*Retention Time*	*Area*	*Peak Width*	*Resolution*	*Tailing*	*PtP S/N*	*RMS S/N*	*No. of Theoretical Plates*
WLP 0% H_2O_2 15 Days - 1	23.66	38298739	0.03	110.64	1.04	0.04	1.26	3393405
	25.15	45193109	0.042	24.15	1.17	0.03	1.06	1944549
WLP 0% H_2O_2 15 Days - 2	23.66	40062544	0.030	111.15	1.06	0.05	1.53	3484874
	25.15	47921002	0.038	25.81	1.17	0.04	1.44	2413522
WLP 0% H_2O_2 15 Days - 3	23.66	36903594	0.028	113.21	1.10	0.04	1.32	3904611
	25.16	38416981	0.044	24.39	1.12	0.03	0.93	1798587

Fabric tearing strength test report before decontamination: CETIQT Test Report Nº. 2220/21.



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Ensaios NBR ISO/IEC 17025
CRL 0005

Relatório de Ensaios CETIQT Nº 2220/21

Revisão: 00

Coordenação de Serviços Laboratoriais **Laboratório Físico**

Cliente: Ingrid Távora Weber (CNPJ: 021.392.734/94)
Endereço: Quadra 203, Nº 9, Sul (Águas Claras), Brasília-DF, CEP: 71939-360
Contato(s): Aline Marcelino Arouca **e-mail(s):** 1020595@etfbsb.edu.br

Interessado: -- (CNPJ: --)
Endereço: --
Contato(s): -- **e-mail(s):** --
Recepção: 27/07/21

Amostra	**Descrição do item fornecida pelo cliente:** Tecido preto da marca Unishell que possui uma composição de 58% para-aramida (kevlar®), 40% meta-aramida (nomex®) e 2% de carbono. - SEM TRATAMENTO	**Código**	2220/21-01	**Coleta em**	--

Ensaio	Resultado	Unidade	Método	Data do Ensaio
Resistência ao rasgo - Teste tongue (ac)	**Urdume = 260,97** **Trama = 218,39** **Descritivo a seguir**	N	ASTM D2261:2013(2017)e1	03/08/21 - 03/08/21

Informações do ensaio - ASTM D2261

Distância entre as garras: 75 mm
Velocidade: 50 mm/min
Tipo de dinamômetro: CRT
Metodologia de cálculo: Média de 5 picos
Software utilizado: Bluehill 3
Condição do corpo de prova: Condicionado
Dimensões da garra: Frontal: 2,5 mm x 7,5 mm Traseira: 2,5 mm x 7,5 mm
C.V. Resistência Urdume (%): 2,95
C.V. Resistência Trama (%): 10,26

Incertezas de medição

Grandeza	U95%	veff	k
Resistência ao rasgo - Urdume (N)	10,1	4,3	2,9
Resistência ao rasgo - Trama (N)	28,8	4,0	2,9

A incerteza expandida de medição relatada é declarada como a incerteza padrão da medição multiplicada pelo fator de abrangência k, de tal forma que a probabilidade de abrangência corresponda a aproximadamente 95%.

O resultado apresentado neste relatório refere-se exclusivamente ao item enviado / entregue, conforme recebido.
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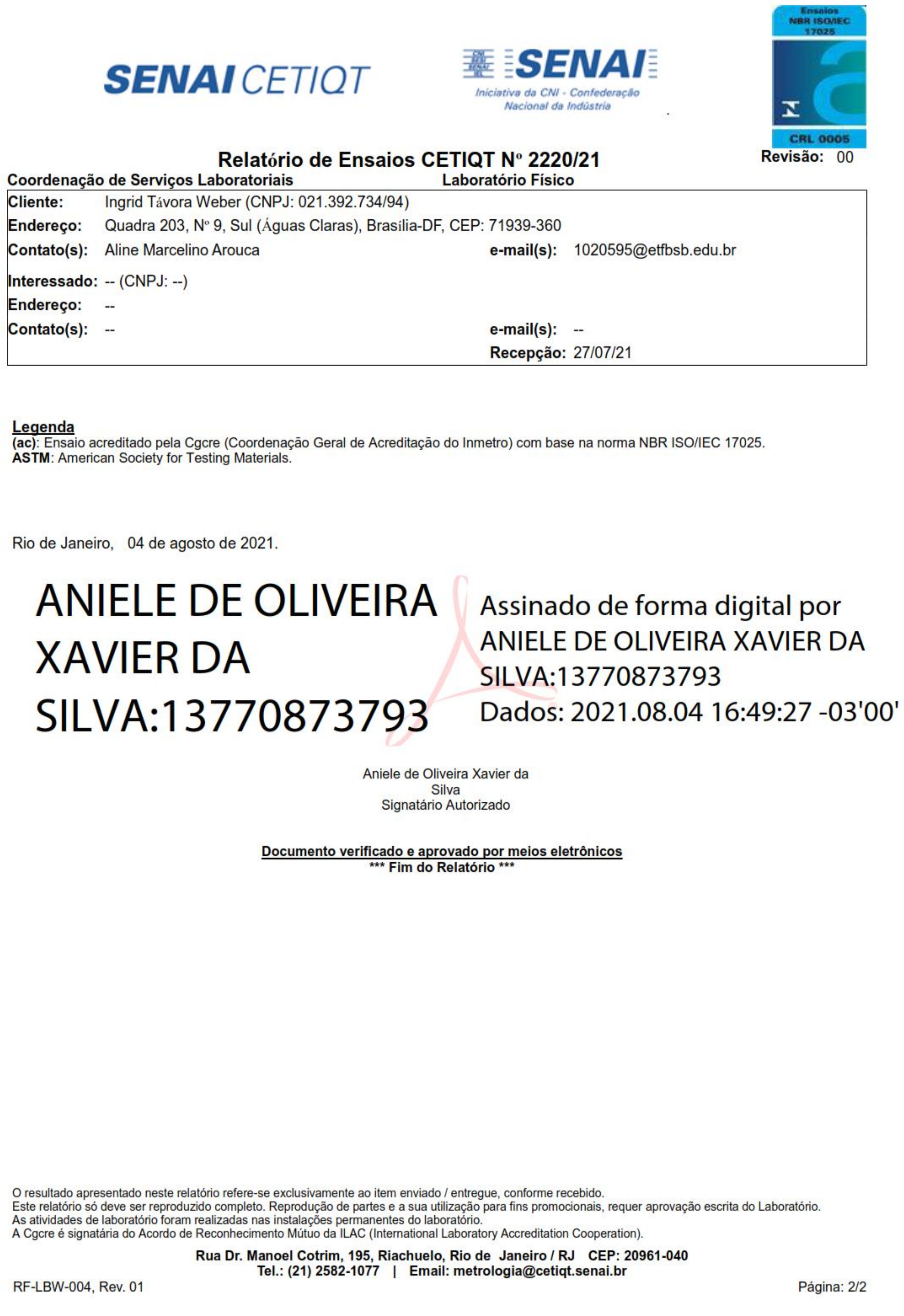
Rua Dr. Manoel Cotrim, 195, Riachuelo, Rio de Janeiro / RJ CEP: 20961-040
Tel.: (21) 2582-1077 | Email: metrologia@cetiqt.senai.br

RF-LBW-004, Rev. 01

Página: 1/2



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Ensaios NBR ISO/IEC 17025
CRL 0005

Relatório de Ensaios CETIQT Nº 2220/21

Revisão: 00

Coordenação de Serviços Laboratoriais **Laboratório Físico**

Cliente: Ingrid Távora Weber (CNPJ: 021.392.734/94)
Endereço: Quadra 203, Nº 9, Sul (Águas Claras), Brasília-DF, CEP: 71939-360
Contato(s): Aline Marcelino Arouca **e-mail(s):** 1020595@etfbsb.edu.br

Interessado: -- (CNPJ: --)
Endereço: --
Contato(s): -- **e-mail(s):** --
Recepção: 27/07/21

Legenda
(ac): Ensaio acreditado pela Cgcre (Coordenação Geral de Acreditação do Inmetro) com base na norma NBR ISO/IEC 17025.
ASTM: American Society for Testing Materials.

Rio de Janeiro, 04 de agosto de 2021.

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Dados: 2021.08.04 16:49:27 -03'00'

Aniele de Oliveira Xavier da Silva
Signatário Autorizado

Documento verificado e aprovado por meios eletrônicos
***** Fim do Relatório *****

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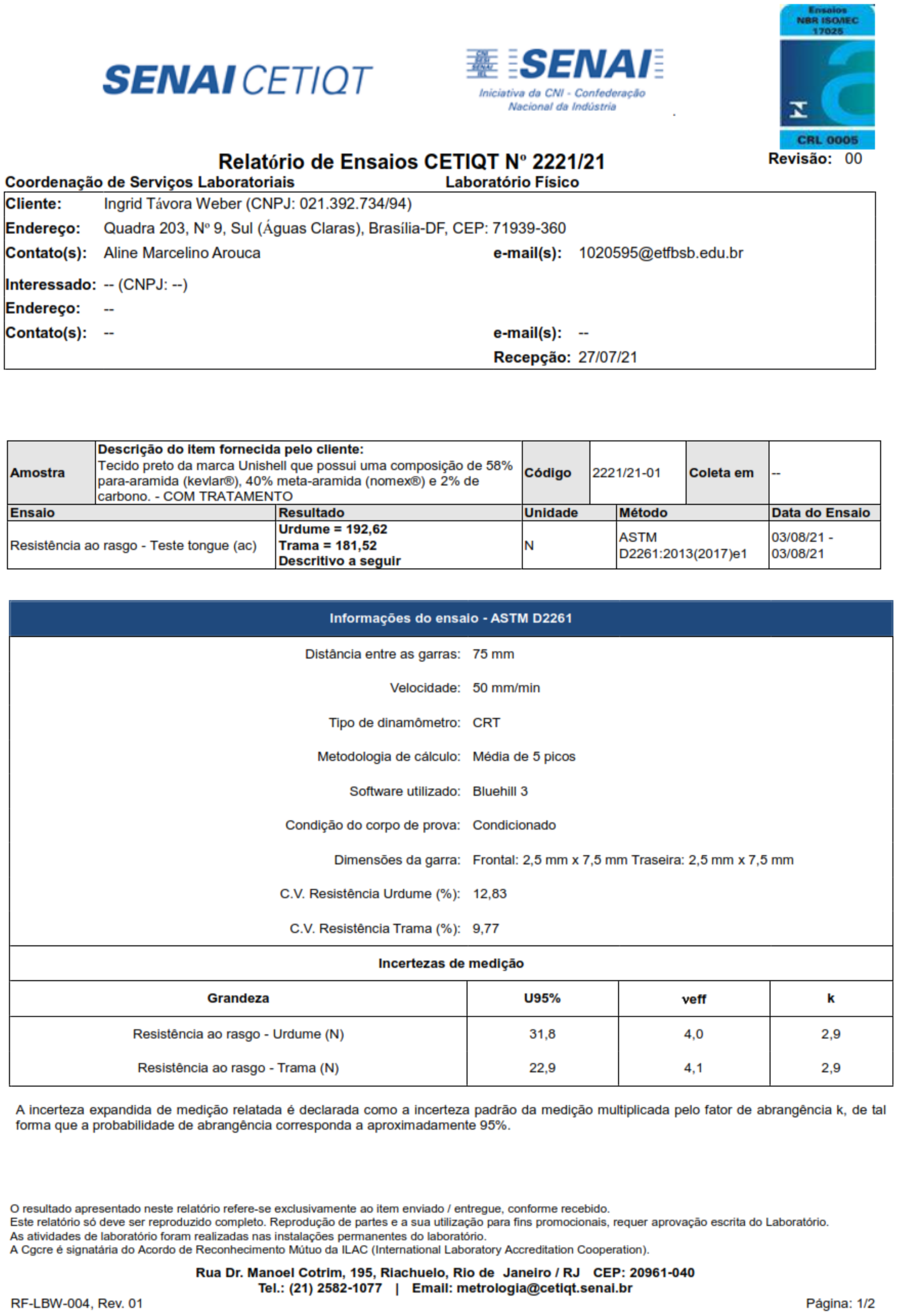
Rua Dr. Manoel Cotrim, 195, Riachuelo, Rio de Janeiro / RJ CEP: 20961-040
Tel.: (21) 2582-1077 | Email: metrologia@cetiqt.senai.br

RF-LBW-004, Rev. 01 Página: 2/2

Fabric tearing strength test report before decontamination: CETIQT Test Report Nº. 2221/21.



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Ensaios NBR ISO/IEC 17025
CRL 0005

Relatório de Ensaios CETIQT Nº 2221/21

Revisão: 00

Coordenação de Serviços Laboratoriais **Laboratório Físico**

Cliente: Ingrid Távora Weber (CNPJ: 021.392.734/94)
Endereço: Quadra 203, Nº 9, Sul (Águas Claras), Brasília-DF, CEP: 71939-360
Contato(s): Aline Marcelino Arouca **e-mail(s):** 1020595@etfbsb.edu.br

Interessado: -- (CNPJ: --)
Endereço: --
Contato(s): -- **e-mail(s):** --
Recepção: 27/07/21

Amostra	**Descrição do item fornecida pelo cliente:** Tecido preto da marca Unishell que possui uma composição de 58% para-aramida (kevlar®), 40% meta-aramida (nomex®) e 2% de carbono. - COM TRATAMENTO	**Código**	2221/21-01	**Coleta em**	--

Ensaio	**Resultado**	**Unidade**	**Método**	**Data do Ensaio**
Resistência ao rasgo - Teste tongue (ac)	**Urdume = 192,62** **Trama = 181,52** **Descritivo a seguir**	N	ASTM D2261:2013(2017)e1	03/08/21 - 03/08/21

Informações do ensaio - ASTM D2261

Distância entre as garras: 75 mm
Velocidade: 50 mm/min
Tipo de dinamômetro: CRT
Metodologia de cálculo: Média de 5 picos
Software utilizado: Bluehill 3
Condição do corpo de prova: Condicionado
Dimensões da garra: Frontal: 2,5 mm x 7,5 mm Traseira: 2,5 mm x 7,5 mm
C.V. Resistência Urdume (%): 12,83
C.V. Resistência Trama (%): 9,77

Incertezas de medição

Grandeza	**U95%**	**veff**	**k**
Resistência ao rasgo - Urdume (N)	31,8	4,0	2,9
Resistência ao rasgo - Trama (N)	22,9	4,1	2,9

A incerteza expandida de medição relatada é declarada como a incerteza padrão da medição multiplicada pelo fator de abrangência k, de tal forma que a probabilidade de abrangência corresponda a aproximadamente 95%.

O resultado apresentado neste relatório refere-se exclusivamente ao item enviado / entregue, conforme recebido.
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Ensaios NBR ISO/IEC 17025
CRL 0005

Relatório de Ensaios CETIQT Nº 2221/21

Revisão: 00

Coordenação de Serviços Laboratoriais **Laboratório Físico**

Cliente:	Ingrid Távora Weber (CNPJ: 021.392.734/94)		
Endereço:	Quadra 203, Nº 9, Sul (Águas Claras), Brasília-DF, CEP: 71939-360		
Contato(s):	Aline Marcelino Arouca	**e-mail(s):**	1020595@etfbsb.edu.br
Interessado:	-- (CNPJ: --)		
Endereço:	--		
Contato(s):	--	**e-mail(s):**	--
		Recepção:	27/07/21

Legenda
(ac): Ensaio acreditado pela Cgcre (Coordenação Geral de Acreditação do Inmetro) com base na norma NBR ISO/IEC 17025.
ASTM: American Society for Testing Materials.

Rio de Janeiro, 04 de agosto de 2021.

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Assinado de forma digital por ANIELE DE OLIVEIRA XAVIER DA SILVA:13770873793
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Aniele de Oliveira Xavier da Silva
Signatário Autorizado

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RF-LBW-004, Rev. 01 Página: 2/2

Unishell® fabric tear strength test report requested by Santanense Workwear: Test Report Nº. 13242/19.

INSTITUTO SENAI
DE TECNOLOGIA
TÊXTIL, VESTUÁRIO E DESIGN

LAFITE – Laboratório de Ensaios Físicos e Químicos Têxteis
Av. Primeiro de Maio, nº 670 – Bairro: 1º de Maio – Brusque – SC – CEP: 88353-202
Fone: (47) 3251-8905 E.mail: lafite@sc.senai.br

RELATÓRIO DE ENSAIO N° 13424/19

Cliente: **COMPANHIA TECIDOS SANTANENSE**
A/C: LEIGIANE
Endereço: RUA DOUTOR ALCIDES GONÇALVES, Nº 1500
SANTANENSE – ITAÚNA – MG
CEP: 35681-184 **Contato:** **(31) 2129-9801**

Data de recebimento: 05/12/2019 **Data de realização do(s) ensaio(s):** 06/12/2019

MÉTODO: RESISTÊNCIA AO RASGO DE TECIDOS PLANOS – NORMA: ASTM D 2261/2017.

CONDIÇÃO DO CORPO DE PROVA: CONDICIONADO

EQUIPAMENTO: EMIC DL2000 COM 75 mm ENTRE GARRAS.

RESULTADOS DOS ENSAIOS

AMOSTRA	RASGO	ITENS	RESULTADOS	U/M
536 TN 1616 UNISHELL	**TRAMA**	Média Força Máxima Aplicada	**25,24**	**Kgf**
	URDUME	Média Força Máxima Aplicada	**22,21**	**Kgf**

Definições:

Rasgo trama – ensaio na direção do urdume – rompimento dos fios de trama.

Rasgo urdume – ensaio na direção da trama – rompimento dos fios de urdume.

OBSERVAÇÕES:

1 – O resultado obtido se refere somente à amostra conforme recebida. Não é emitido parecer de comparação com qualquer tipo de padrões ou especificações (só quando solicitado / fornecido pelo cliente) e não pode ser reproduzido parcialmente.
2 – Ambiente: Temperatura = (20 ± 2) °C e UR = (65 ± 4) %.
3 – Orçamento 979/2019.

--X--

Brusque, 12 de Dezembro de 2019.

FM-BRU-004 Revisão 02 – 19/09/2019
Aprovador: Adécio Gamba
Página 1 de 1

Documento eletrônico assinado digitalmente.
Validade jurídica assegurada conforme
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Data: 13/12/2019 12:13:30
CPF: 887.308.839-20
Nome: ANICEIA PATRICIA DA
CUNHA SCHMITT:88730883920

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CERTIFICATE OF ACCEPTANCE

Certificate of acceptance for the manuscript (**ijerph-1782937**) titled:

White Light-Photolysis for the Removal of Polycyclic Aromatic Hydrocarbons from Proximity Firefighting Protective Clothing

Authored by:

Aline Marcelino Arouca; Victor Emmanuel Delfino Aleixo; Maurício Leite Vieira; Márcio Talhavini; Ingrid Távora Weber

has been accepted in *Int. J. Environ. Res. Public Health* (ISSN 1660-4601) on 23 June 2022

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Article

White Light-Photolysis for the Removal of Polycyclic Aromatic Hydrocarbons from Proximity Firefighting Protective Clothing

Aline Marcelino Arouca [1,*], Victor Emmanuel Delfino Aleixo [2], Maurício Leite Vieira [3], Márcio Talhavini [3] and Ingrid Távora Weber [2]

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[2] Laboratory of Inorganic and Materials (LIMA), Chemistry Institute, University of Brasilia—UNB, Brasilia 70904-970 , Brazil
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Abstract: The presence of polycyclic aromatic hydrocarbons (PAHs) on firefighters' personal protective equipment is a concern. One form of preventing from these compounds is to decontaminate proximity firefighting protective clothing (PFPC). Traditional decontamination methods do not promote total removal of pollutants and alter the properties of PFPC. The objective of this work was to evaluate the effectiveness of white light-photolysis (WLP), an advanced oxidation process (AOP), for removing PAHs from PFPC, while maintaining the integrity of the fabric fibers. Experiments were carried out, varying reaction time and concentration of H_2O_2. With WLP (without H_2O_2), it was possible to remove more than 73% of the PAHs tested from the outer layer of PFPC in 3 days. The WLP provided the greatest removal of PAHs, compared with the most common mechanical decontamination techniques (laundering and wet-soap brushing). The fibers' integrity after exposure to the white light was evaluated with infrared spectroscopy and scanning electron microscopy/energy dispersive X-ray spectrometry. In addition, a tearing strength test was performed. No remarkable fabric degradation was observed, indicating a possible, routine-compatible, simple, and inexpensive method of decontamination of PFPC, based on photolysis, which is effective in the degradation of PAHs and maintains the integrity of fabric fibers.

Keywords: photolysis; polycyclic aromatic hydrocarbons (PAHs); firefighters; personal protective equipment (PPE); proximity firefighting protective clothing (PFPC); advanced oxidation process (AOP)

check for updates

Citation: Arouca, A.M.; Aleixo, V.E.D.; Vieira, M.L.; Talhavini, M.; Weber, I.T. White Light-Photolysis for the Removal of Polycyclic Aromatic Hydrocarbons from Proximity Firefighting Protective Clothing. *Int. J. Environ. Res. Public Health* **2022**, *19*, 10054. https://doi.org/10.3390/ijerph191610054

Academic Editors: Gassan Hodaifa, Antonio Zuorro, Joaquín R. Dominguez, Juan García Rodríguez, José A. Peres and Zacharias Frontistis

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1. Introduction

Firefighting is a high-risk activity, affecting the physical and mental health of these professionals. The International Agency for Research on Cancer (IARC) has classified firefighters' exposure to toxic materials as Group 2B, that is, possibly carcinogenic to humans [1]. As well as the obvious effects of combustion of hazardous materials, the contamination of firefighters' proximity protective clothing may promote danger to their health as well.

One of the main compounds that is formed during the combustion and pyrolysis process of a material are the polycyclic aromatic hydrocarbons (PAHs) [2,3]. PAHs represent a class of complex organic chemicals with more than 100 compounds containing two or more aromatic rings condensed in different ways in their structures [4]. PAHs can be formed by different pathways, as in an oil spill or oil seepage. The incomplete combustion of organic matter and fossil fuels is the most prominent source of PAHs in the environment [5]. The concern about the presence of these compounds in fire residues is due to the fact that many PAHs are considered carcinogenic, mutagenic, and teratogenic [6,7].

https://doi.org/10.3390/ijerph191610054

CHAPTER 4

FINAL CONSIDERATIONS

FINAL CONSIDERATIONS

The purpose of this thesis was to study three themes related to the firefighter profession and occupational health. It is known that when firefighting, firefighters encounter several toxic compounds. Because of that, these professionals have a higher risk of developing cancer, such as lung, prostate, brain, kidney, and testicular cancers. In addition to direct contamination of the firefighter with these pollutants, the firefighter can be contaminated via indirect, where the professional comes into contact with the compounds deposited in personal protective equipment (PPE). Therefore, the decontamination of PPE must be carried out regularly, in order to reduce the risk of developing cancer.

Initially, issues related to PPE cleaning and storing, firefighter cancer risk awareness were evaluated. The study was carried out with the development of a form with 23 questions. Two corporations, Military Firefighters of the Federal District (CBMDF) and Military Fire Brigade of Pernambuco (CBMPE), participated in the survey, with 79 and 58 answers, respectively. Several questions were evaluated, from age to PPE storage location after use in firefighting and where firefighting turnout gear are washed. We observed good awareness related to the risk of cancer and basic skills to minimize those risk, despite the lack of structure of the fire battalion and incompatibility with the work routine. The main problems found are related to PPE cleaning in inappropriate places (firefighters' home), inadequate storage and low cleaning frequency. Also, a lack of information, training and guidance inside fire departments to reduce cancer risk was pointed out by participants.

In the second stage of this thesis, the pollutants deposited in firefighters during firefighting were evaluated. Among the toxic compounds described in the literature as by-products of the incomplete combustion process, an important class is the polycyclic aromatic hydrocarbons (PAHs). Therefore, the focus of the work was to evaluate the presence of PAHs in Brazilian firefighters’ personal protective equipment following training exercise of fire combat. The training exercise was carried out in a simulated fire scenario, performed in a shipping container. For the exercise 10 firefighters and 2 instructors participated in the exercise and wipe sampling were collected in 4 different points, shoulder (P1), sleeve (P2), chest (P3) and gloves (P4), in two different time, before-training exercise (BT) and after-training exercise (AT). Each swab was extracted with acetonitrile and analyzed with GC/MS. Of the 16 compounds evaluated the following PAHs were found: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene and pyrene, all in pre-fire and post-fire samples. Naphthalene and phenanthrene were the main pollutants found, having a concentration which varied from 0.007 up to 1.066 $\mu g.mL^{-1}$. Comparing all points sampled, they presented similar patterns. In addition to the presence of these compounds in concentrations close to the limit allowed by monitoring agencies, an important factor evidenced in the experiments is that the fire instructor presented a greater/quantity variety of deposited PAHs when compared to other participants. These professionals, because they carry out a greater number of combats and also because they remain in contact with the flames for a longer time, end up exposing themselves more to these pollutants than a firefighter who carries out residential combats, who perform a smaller number of calls.

Finally, in the last chapter, a technique for the decontamination of firefighter turnout gear contaminated with PAHs was developed, based on an advanced oxidative process (AOP). The method would be an alternative to the physical decon processes already used by firefighters and was evaluated white lamp (WLP) and UV lamp (ULP) photolysis in the degradation of two analytes: pyrene and 9-methylanthracene. Also, three H_2O_2 concentrations (0%, 0.35% and 3.5%) and two reaction times were tested (1 and 3 days). The best results were obtained with the WLP (0% H_2O_2), after 3 days, the method promoted the removal of 81±8% of both PAH following a pseudo-second-order rate. The formed by-products were identified and no PAHs derivatives more harmful than the original PAHs were formed. All by-products formed during the reaction decreased with the course of the reaction, being consumed by the photolysis reaction. Regarding the fabric analysis, the protective clothing outer shell fabrics treated (without the PAH) were evaluated to assess whether the photolysis decon promoted the deterioration of the fibers. The chemical and morphology of the fibers were evaluated with optical microscopy, FTIR/RTA, SEM/EDS and tearing strength. No changes were obtained in the spectra that could indicate the breakdown of fiber polymers and the reduction showed in the tearing strength test is correlated with the partial removal of fabric’s water repellant coating.

The WLP decon was compared with the with laundering decon and wet-soap brushing decon on three-layer fabrics samples. Photolysis showed a removal of 73% of the deposited PAHs, while laundering removed 44% and wet-soap brushing 32%. All the results obtained in this thesis show that the 3 days WLP (without H_2O_2) is an efficient decon method for the removal of PAH deposited in the proximity firefighting protective clothing, maintaining fabric´s integrity and properties that has several advantages than the most used physical decontamination techniques.

Thus, the three topics evaluated in this thesis are extremely important for the occupational health of firefighters, and address topics that are not yet discussed within the corporation/state. There is still a long way of studies and analysis ahead, but this research results are promising and can promote an improvement in the lives of these professionals.

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Brasília, 11 de dezembro de 2023.

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