

# Ensuring firefighter safety and resource preservation from contamination in demolition building fires

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## Abstract

Research characteristics and define toxic substances that remain in emergency clothing after fires in abandoned and demolition buildings. As a basic component of the integrated rescue system, members of the Fire and Rescue Service may be primarily or secondarily exposed to the effects of dangerous substances that penetrate the body as part of intervention activities. Personal protective equipment (PPE) used by firefighters can be characterized as a potential source of hazardous exposure to toxic contaminants commonly found and released during fires. The research task was to detect these contaminants in individual samples based on gas chromatography (GC) and subsequently to determine the decontamination methods of firefighters and PPE after an intervention. Based on a real intervention in an abandoned and demolished building where there was a fire, firefighters from individual fire stations intervened, where, as stated in the research, they intervened in the mentioned protective equipment. The amount of dangerous substances was determined based on gas chromatography in the Control and Chemical Laboratory of the Ministry of the Interior in the village of Jasov. The stated procedure was used to determine the amount of residual hazardous substances on emergency clothing and the procedures for possible elimination of the hazard.

## Keywords

Contamination; Firefighter; Toxic substance; Emergency clothing; Gas Chromatography; Decontamination



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## Introduction

More and more research and evidence indicate that firefighters have an increased risk of developing cancer and other diseases compared to the general population. This increased risk may be related to firefighters' occupational exposure to toxic fire fumes [LeMasters et al., 2006; Hull et al., 2009; Wolffe et al., 2023].

As for individual research, due to exposure to toxic combustion products, these hazardous substances remain not only on the PPE but due to the use of only one emergency clothing during the performance of the service, these hazardous substances are transferred to the fire stations and finally to the surface of the firefighters's body and thus also to the organism. These contaminants are receiving increasing attention worldwide, and they focus on decontamination procedures that aim to minimize the exposure of firefighters and thereby reduce the incidence of cancer [Stec and Hull, 2010; Horn et al., 2022].

In the Slovak Republic, firefighting PPE consists of an emergency jacket, emergency trousers, emergency shoes, helmet, gloves, firefighter's hood, and an autonomous breathing apparatus with an open circuit – pressure relief, while depending on the type of danger during an intervention, the PPE may differ. In addition to this emergency clothing, station uniforms, such as T-shirts and trousers, are classically worn underneath. While the above PPE is designed to protect against several hazards (heat, cold, surface wetting, radiant heat, overheating, etc.), more and more research and literature question the effectiveness of this garment when it comes to exposure to toxic and carcinogenic substances or a complex contaminant [Gill and Britz-McKibbin, 2020; British Standards Institution, 2022; British Standards Institute, 2021; National Fire Chiefs Council, 2022].

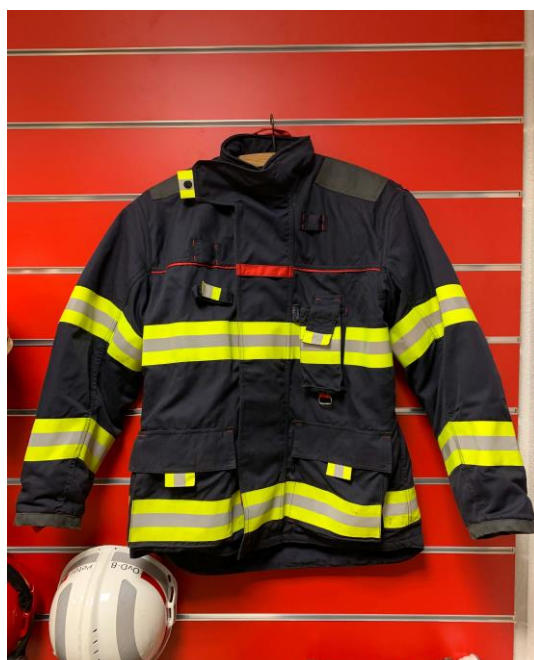


Fig. 1. Emergency clothing of the Fire and Rescue (source: elaborated by authors)

For example, according to Mayer et al., there is a potential diffusion of toxic gases and vapors through the emergency clothing of firefighters. In contrast, the concentration of benzene, toluene, and naphthalene on said clothing was proven, and these concentrations corresponded to the concentrations measured during the fire itself. Research and studies have also documented the presence of toxic substances and carcinogens (including polycyclic aromatic hydrocarbons - PAHs), which penetrated through the interfaces of emergency clothing and PPE and were detected directly on the skin of intervening firefighters [Mayer et al., 2022; Mayer et al., 2020].

Currently, there is no legal standard or legislation in force that requires PPE commonly used in response to protect against chemical or biological agents (meaning normal response clothing), which requires detailed research to lead to innovations in the field protection of the body against carcinogenic, toxic, or biological substances. In addition to the classic effect of contaminants on firefighters during a fire, there are also other ways in which contaminants can affect firefighters, such as handling contaminated PPE, storing contaminated PPE, handling during individual cycles of decontamination and washing, etc. [Fent et al., 2020; Kirk a Logan, 2015; Mayer et al., 2019; Betuš et al., 2023].

Recent studies conducted by Banks et al. and Gill et al. also focused on levels of contaminants in the air at individual fire stations, where firefighters spend a significant amount of their free time. Measured higher

concentrations of polycyclic aromatic hydrocarbons, organophosphorus flame retardants, and polybrominated diphenyl ethers were found in air and dust collected from fire stations, probably brought back to the station on contaminated PPE or equipment after interventions. Particular attention has recently been paid to fluorinated compounds found in fire stations, as these compounds are not only used in firefighter PPE but are a major component of some firefighting foams [Banks et al., 2021; Gill, 2020; Stec et al., 2018; Young et al., 2021; Hall et al., 2020].

Also, epidemiological studies conducted by LeMasters et al. proved an increased risk of cancer in firefighters. In 2010, the International Agency for Research on Cancer (IARC) classified firefighting as a possibly carcinogenic activity (group 2B). Additional studies that were conducted after the IARC meeting further identified excess cancer risk for firefighters, with meta-analyses providing additional information on increased risk for specific types of cancer, including melanoma, testicular, bladder, prostate, colon, and rectal cancer [Ma et al., 2006; Stang et al., 2003; Youakim, 2006; Soteriades et al., 2019; Lee et al., 2020;].

Although there may be many causes of increased cancer risk, Daniels et al. found a relationship between firefighting and leukemia, as well as long-term exposure to fire and lung cancer, suggesting that the increased cancer risk in firefighters is due to both their exposure to fire and the effects of combustion products [Lee et al., 2020; Daniels et al., 2014; Lee et al., 2020; Thai et al., 2015; Casjens et al., 2020].

Most importantly, in June 2022, 25 scientists met at the International Agency for Research on Cancer (IARC) in Lyon, France, to complete an assessment of the carcinogenicity of firefighter exposure. Firefighter exposure has been classified as "carcinogenic to humans" (group 1) based on "sufficient" evidence of cancer in humans. The task force concluded that there is "sufficient" evidence of mesothelioma and bladder cancer in humans. In humans, there was "limited" evidence for colon, prostate, and testicular cancer and for melanoma and non-Hodgkin's lymphoma. There was also "strong" mechanistic evidence that firefighter exposure exhibits the following key characteristics of carcinogens in exposed humans: "is genotoxic," induces epigenetic changes, induces oxidative stress, induces chronic inflammation, and modulates receptor-mediated effects [Nikalje, 2017; Jacobs et al., 2013; Zhang et al., 2023; Tomaskova et al., 2022].

Regarding fires in demolition buildings or similar structures, it is generally documented that exposures to toxic substances resulting from the IARC include known carcinogens (group 1), probably known carcinogens (group 2A), or possible (group 2B) carcinogens, including benzene (group 1) and naphthalene (group 2B). Firefighter exposure to volatile organic compounds such as benzene has been demonstrated through air samples taken during structure fires and immediately after fire suppression. Several studies have also documented increased inner exposure to benzene by analyzing benzene in firefighters' breath or benzene metabolites in urine samples after firefighting. However, it should not be forgotten that not all types of fires are identical in terms of the amount of toxic and carcinogenic substances released. It should be taken into account that during a fire in buildings, there are different types of combustible materials, and different concentrations of dangerous substances are released when they burn. This results in different concentrations of these dangerous substances [Jalilian et al., 2019; International Agency for Research on Cancer, 2010; Jankovic et al., 1991; Bolstad-Johnson et al., 2000; Caux et al., 2002; Fent et al., 2020; Wallace et al., 2019].

A firefighter's hood is considered one of the most vulnerable components of PPE in terms of exposure. Besides the new types of PPE, a recent study found that repeated wear and subsequent washing can affect protective properties concerning physical and chemical hazards. A study to detect PAH contamination confirmed high levels of PAHs in the neck area despite protective measures designed to reduce the penetration of contaminants into the skin [Rosting and Olsen, 2020; Skvarekova et al., 2021; 2020; Horn et al., 2021].

Kirk and Logan found that PAH concentrations inside the mantle were as high and sometimes higher than those outside the mantle, while Wingfors et al. found that total PAHs were 146 times lower when measured inside the base layer than on the surface of the firefighter's coat. Chemicals that are deposited on thin areas of the skin, such as the neck, are generally absorbed more quickly than on thick areas of the skin. While some less volatile compounds, such as higher molecular weight PAHs bound to solid particles, can be rapidly deposited on the skin and absorbed transdermally, benzene and lower molecular weight PAHs usually remain in the gas phase and up to 1% of these vapors can be absorbed through the skin. In addition, these volatile compounds can condense and be absorbed through the skin, especially if they are trapped on the skin and cannot evaporate [Kirk and Logan, 2015; Wingfors et al., 2018; VanRooij et al., 1993; Wester and Maibach, 2000].

Objectives of this study:

- Quantification of the concentration of PAH inside the emergency vest, in the inner part of the firefighter's helmet, and in the outer part of the emergency vest after intervention during firefighting,
- To quantify the residual amounts of PAHs after washing emergency clothing in a laundry,
- To investigate the relationship between internal and external surfaces and residual PAHs [Kirk and Logan, 2015; Wingfors et al., 2018; Tomaskova et al., 2022].

## Materials and Methods

### Materials

The study itself was about firefighter protective clothing, as shown in Figure 1. 100 samples of 0.1 x 0.1 m were cut from the emergency clothing, which was previously normally washed in the fire station laundry room, and these samples were cut from the top layer jacket and also the top layer of firemen's trousers. The following detergents were used (Figure 2):

- Deryal Rent,
- Ottalin Peracet,
- Hydrob FC.



Fig. 2. Detergents for washing emergency clothing (source: elaborated by authors)

Firefighters' emergency clothing is a classic personal protective equipment that is used to respond to all types of emergencies. The emergency clothing that was used as a sample was 5 years old, where in five years; it was worn for interventions such as fires and traffic accidents, and after each fire, at the end of the service, it was washed with the detergents listed below. Given that the fire station in Košice has an average number of interventions for the year 2000. Firefighters perform their work in three shifts, while one shift has 30 firefighters. The average number of fires from the total number of interventions is 50 percent, and the rest are technical interventions. From the above, it follows that with the stated age of emergency clothing and the number of interventions, the clothing that was on duty for one firefighter was used an average of 300 times during fires of all types. The emergency clothing is a two-piece, multi-layered suit intended primarily for firefighters deployed for firefighting and rescue work. Design solution: The suit consists of an upper garment - coat, trousers, and a lower garment - removable inner inserts (moisture thermal barrier). Material composition: Outer layer: 98% aramid 2% antistatic fiber with RipSTop grid for higher strength, 220g/m<sup>2</sup> Removable thermoregulation insert: moisture barrier FR PES/PU+ non-woven fabric + FR lining) 440 g/m<sup>2</sup>.

The mentioned detergents disinfect and discolor soiled clothes and have a high ability to remove pigment and impurities. Textiles, in this case, emergency clothing, will be stain-resistant when in use and will also be able to repel water and oil [Thrall et al., 2000]. In one firefighting shift, all 30 firefighters working at the fire station in Košice were informed about the research. One change that agreed with the mentioned research was selected. Each firefighter received six samples, put two of them into the inner pocket of the firefighter's coat, then put two samples into the outer pocket and two into the firefighter's helmet, as shown in Figure 3.

Obviously, the exit does not include all 30 firefighters, but according to the type of emergency broadcast by an operational officer, the number of intervening firefighters will be defined in the article below.

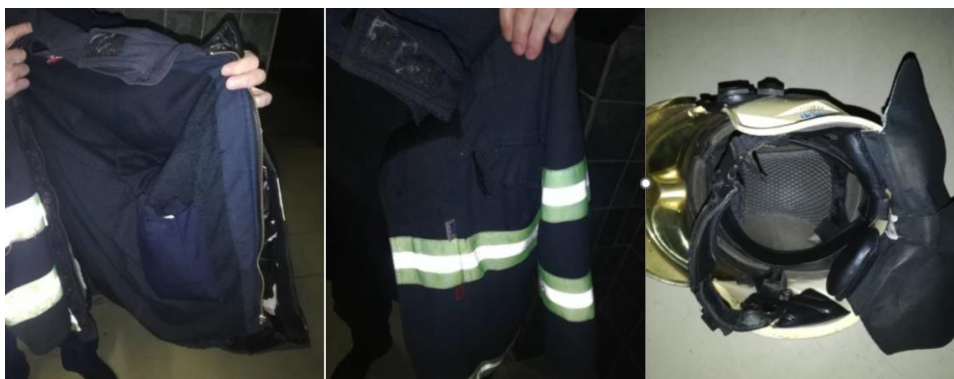


Fig. 3. Placement of samples (source: elaborated by authors)

Samples were taken after the fire. Sample no. 1 from the inner pocket was placed in a 10 ml vial, sample no. 2 from the outer pocket was placed in a 10 ml vial, and the last sample no. 3 from the emergency helmet was also inserted into a crimping vial (Figure 4). After the intervention, the other samples were washed and dried together with the firefighter's clothing. Subsequently, these samples were placed in 10 ml glass crimp vials and ziplock bags after these processes and transported to the chemical laboratory for research [Hwang et al., 2021].



Fig. 4. 10 ml vial, crimp caps, and pliers (source: elaborated by authors)

### Selection and implementation of a suitable method for measuring toxic substances

The method used to measure PAHs consisted of attaching samples of the same type of garment fabric to the inside of the outer pocket of a fireman's coat, the inside of the inside pocket of a jacket, and the inside of a helmet. The samples had dimensions of 0.1 m x 0.1 m. Samples of the given dimensions were exposed to smoke. After the fire, samples were collected and stored in glass crimp vials and clear, resealable plastic zip-top bags. The samples stored in this way were prepared for extraction in N-hexane and subsequent analysis using a chromatograph - Agilent 5975T LTM GC/MSD [Wei et al., 2023; Robert Koch-Institut, 2017; Pooja et al., 2022; Kaur and Sharma, 2018; Lehotay and Hajšlova, 2002].

Chromatography is known as a set of techniques that are used to separate components in a mixture. The separation of these elements that we want to find out is based on the difference between the numbers of individual sections of these two phases. This research uses gas chromatography with a single quadrupole mass spectrometer, which has many advantages for analyzing small and volatile molecules such as steroids, fatty acids, and hormones. It can separate complex samples, quantify analytes, and determine trace levels of organic contamination. This technique can be used to investigate liquid, gas, and solid samples [Wei et al., 2023; Robert Koch-Institut, 2017; Pooja et al., 2022; Kaur and Sharma, 2018; Lehotay and Hajšlova, 2002].

### Agilent 5975T LTM GC/MSD Chromatograph

The Agilent 5975T LTM GC / MSD is the first commercial portable GC / MS system that delivers high reliability, performance, and quality (Figure 5). The GC / MS system guarantees the best performance and results anywhere, whether in the laboratory or the field.

Advantages:

- Weight range 1.8 to 1050μ,
- Fast heating (up to 1,200°C / min.),
- Contains anti-vibration elements,
- Ideal for use in mobile laboratories,
- Faster on-site analysis,
- Uses Agilent's proprietary LTM technology,
- Enables faster GC analysis and higher sample throughput,
- LTM technology shortens GC cycle times and makes it easier for them to deal with different and sometimes complex analytical challenges,
- Model 5976T uses DRS (Deconvolution Reporting Software) and RTL (Retention Time Locking) database, which guarantees fast analysis of compounds in the field,
- One system suitable for both laboratory and field use,
- Reliable results anytime, anywhere [Nikalje, 2017].

The Agilent 5975T's on-site capability significantly reduces time to results. The results are known in a shorter time frame, which is decisive in cases where life, health, and safety may be threatened. Since the samples are processed on-site, there can be no problem of degradation and contamination of the sample during transport or storage [Nikalje, 2017].



Fig. 5. Agilent 5975T LTM GC/MSD Chromatograph (source: elaborated by authors)

### GC-MS/MS analysis

The identification and quantification of individual PAHs were performed by GC–MS/MS due to the high sensitivity and specificity of this analytical technique for contaminated soil samples. An Agilent Technologies 5975T LTM GC/MSD gas chromatograph (GC) equipped with an Agilent PAL 120 autosampler and a 10 µl injection system was used for PAH separation.

### Description of the fire location

The fire occurred in the abandoned area of the former Východoslovak mills and bakery in Košice. The complex was put into operation in 1957 and was considered the largest complex in Central Europe (Figure 6).



Fig. 6. Original photo of the object after the end of operation [Košice - abandoned mill]

Gradually, in 2007, the company went bankrupt and changed employers several times, while in 2008, production stopped completely, and the building was sold to shareholders living in Hungary. Until 2015, the building was guarded by a private security service, and from that year, it gradually began to deteriorate, and the homeless slept there.

The fire started in the administrative part of the building on the 2nd above-ground floor (Figure 7), where the floor plan dimensions of the office where the fire started were 3.9 x 4.2 m and the headroom was 3 meters (Figures 8 and 9). The fire was reported to the HaZZ operations center at 11:28 a.m. and completely extinguished at 1:44 p.m.

The intervention was attended by 9 firefighters with three pieces of equipment, a Mercedes Benz Vario and two Iveco Trakker – fire trucks. During the intervention itself, all samples were exposed to the same fire. As for the building itself, the cause of the fire, determined by the fire investigator, was the handling of an open fire, and the area affected by the fire contained classic office equipment such as cabinets, chairs, and a sofa set. The fire extinguishing itself was carried out with one attack C jet (52 mm hose diameter) with a compact flow line and a water flow of 200 liters per minute and a high-pressure jet (25 mm high-pressure hose diameter) with water consumption of 250 liters per minute and a pressure of 4 MPa. Firefighters intervened with self-contained breathing apparatus, where the line was pulled up the staircase and water consumption to extinguish the fire and cool the surrounding structures completely was 6,000 waters. At 4:00 p.m., the clothes, including the pinned samples, were

put into the washing machine. The washing cycle, including drying, lasted approximately 90 minutes. Subsequently, samples were taken from the clothing. The procedure was the same as after the fire. All samples were sorted, counted, and checked for correct labeling. The firemen, who had textile samples pinned to their clothing, were taken after the fire was extinguished using latex gloves, placed in hermetically sealed crimping 10 ml test tubes and handed over for analysis to the Control Chemical Laboratory in Jasov.



Fig. 7. The building where the fire took place (source: elaborated by authors)



Fig. 8. The space after the fire (source: elaborated by authors)

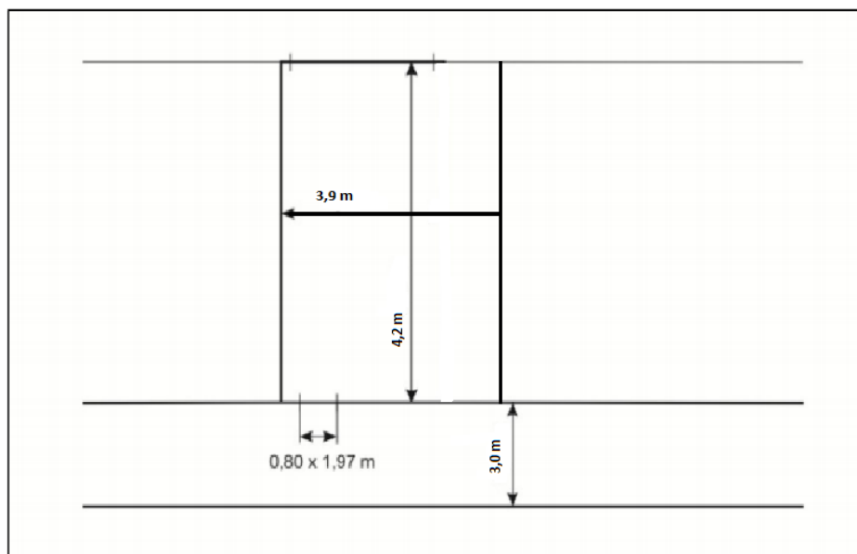


Fig. 9. The building where the fire took place (source: elaborated by authors)

## Decontamination procedure

After the end of the intervention and liquidation of the fire, firefighters's clothing is normally used, without decontamination procedures, at all fire stations in Slovakia.

After finishing the intervention, the firefighters put the used materials into the vehicles, which was also the case in this case, and they got into the fire engines in emergency clothing. Upon arrival, in this case, samples of emergency clothing were taken from the above-described places in vials and taken to KCHL in Jasov.

The clothing used in the fire was left in the vehicles until the following morning when working hours ended. During the aforementioned day, these firefighters no longer participated in the liquidation of any other extraordinary events. In the event of other fires, they would intervene in the same firefighter's clothing. The washing procedure was as follows: 5 upper parts of emergency clothing were placed in the Miele Professional PT 8257 washing machine and were disinfected with Ottalin Percet at a temperature of 60°C and a washing time of 20 minutes (Figure 10). Dosing was automatic, as determined by the manufacturer of each device. Subsequently, the outer garments were washed at a temperature of 60°C and a washing time of 60 minutes with Derval Rent detergent, where the dosing is also automatic. The subsequent impregnation lasted 15 minutes at 40°C for all five outer garments. 5 pieces of outerwear were dried in the dryer at 40°C for 45 minutes. They were then stored in the dressing room for further use.



Fig. 10. (a) Dryer at the fire station; (b) Washing machine at the fire station (source: elaborated by authors)

## Results

The analysis of individual samples was carried out in the Chemical Control Laboratory of Civil Protection in Jasov. The following procedures were performed for the evaluation of the samples:

- Tools used in the laboratory (10 ml pipette, Pipette divided into 1 ml, Vial 1.8 ml + caps with PTFE set, Shaker),
- Chemicals (N-hexane for GC (gas chromatography)).

10 ml of N-hexane was pipetted into the sample vial with the collected samples, the sample vial was thoroughly closed, and extraction was carried out for 60 minutes with an intensity of 400 oscillations per minute. Subsequently, the samples were left at rest throughout the night. 1 ml of the extract was subsequently taken, transferred to a 1.8 ml vial, and analyzed on a gas chromatograph with GC-MS mass spectrometry (Gas chromatography-mass spectrometry).

Method of injection:

- the volume of sample vial 1  $\mu$ l,
- injection temperature 280°C,
- pulse splitless, pulse pressure 140 kPa during 0.4 min.

GC measurement parameter:

- column, HP-5MS – stationary phase - 5% Phenylmethylsiloxane, length 30 m, diameter 250 $\mu$ m,



- carrier gas – helium,
- column temperature program:  $T_{\text{init}} = 80^{\circ}\text{C}/1 \text{ min}$ ; gradient  $20^{\circ}\text{C}/\text{min} - 130^{\circ}\text{C}$ ;  $5^{\circ}\text{C}/\text{min}$ ;  $t_{\text{fin}} = 320^{\circ}\text{C}/5 \text{ min}$ ,
- He flow 0.8 ml/min (constant flow mode).

#### MS measurement parameter:

- ion source temperature:  $205^{\circ}\text{C}$ ,
- quadrupole temperature:  $150^{\circ}\text{C}$ ,
- transferline temperature:  $280^{\circ}\text{C}$ ,
- measurement range: 30 – 300 m/z,
- data: fullscan, EI+, energy 70 eV.

#### Measuring device and SW evaluation:

- GC type: Agilent 5975T LTM GC / MSD,
- injector: Agilent Technologies 7683 B,
- detector: MS detector Agilent technologies 5975,
- evaluation software: MSD Chemstation D. 02. 00. 275,
- NIST 2005 SpectralLib database.

Analytes were separated by a DB-5 ms ultra inert capillary column comprising a first column of internal diameter 0,25 mm, length 30 m and thickness 0,25  $\mu\text{m}$  and a second column of internal diameter 0,25 mm, length 25 m and thickness 0,25  $\mu\text{m}$ . The analysis involved pulsed splitless mode with an injection volume of 2  $\mu\text{L}$ . The oven temperature was programmed as follows: initial temperature at  $50^{\circ}\text{C}$  (hold 1 min), then  $25^{\circ}\text{C min}^{-1}$  to  $325^{\circ}\text{C}$ , held for 5,2 min. High-purity helium ( $>99.999\%$ ) was used as carrier gas with a flow rate of  $1.4 \text{ ml}\cdot\text{min}^{-1}$  in the first column and  $1.5 \text{ ml}\cdot\text{min}^{-1}$  in the second column. Detection of the analytes was performed by employing an Agilent Technologies triple quadrupole mass spectrometer operating in Multiple Reaction Monitoring mode. The  $\text{N}_2$  collision cell and He quench gas were set at  $1,5 \text{ ml}\cdot\text{min}^{-1}$  and  $2,25 \text{ ml}\cdot\text{min}^{-1}$ , respectively. The GC-MS inlet temperature was set at  $90^{\circ}\text{C}$  for 0,01 min, then  $900^{\circ}\text{C min}^{-1}$  to  $325^{\circ}\text{C}$  until analysis. The transfer line was set at  $325^{\circ}\text{C}$ . The ion source temperature was set at  $350^{\circ}\text{C}$ , and both quadrupole 1 and quadrupole 2 were set at  $205^{\circ}\text{C}$ . Quantification of the analytes employed the integrated peak area ratio of the target ion to the internal standard. The PAH analytes were identified based on target and retention time order.

## Analysis of results and measurements

This section summarises the measurement results described in the previous section. The primary examined PAHs were not found in any of the samples. The chromatograms below show which substances were measured on the examined fabrics.

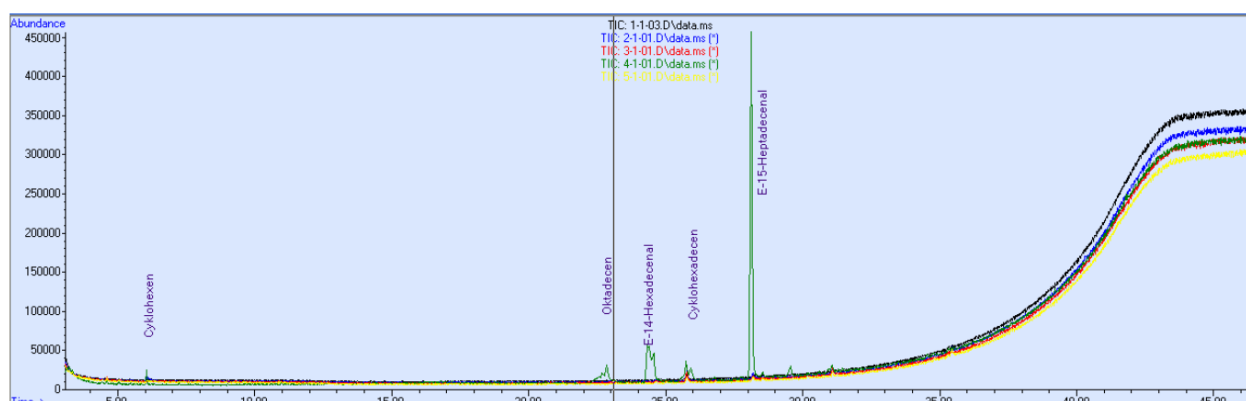


Fig. 11. Chromatogram - unwashed clothes, chest (source: elaborated by authors)

Based on the first evaluated chromatogram (Figure. 11), the x-axis is the time of evaluation of the unwashed emergency clothing using gas chromatography, and the y-axis is the level of the measured substances detected during the evaluation. The value of the measured substances on the y-axis depends on the time during which the quantity of these substances flows through the carrier gas. From the mentioned chromatograph, it follows that the following substances were measured on the unwashed clothes, specifically on the chest where the samples were placed:

- Cyclohexane was recorded at the 6<sup>th</sup> minute, where the value reached 500 units in 10 ml of N-hexane,

- Oxadecene was recorded at the 23<sup>rd</sup> minute, where the value reached 4900 units in 10 ml of N-hexane,
- E-14 Hexadecanal was recorded at the 24<sup>th</sup> minute, where the value reached 6000 units in 10 ml of N-hexane,
- Cyclohexadecene was recorded at the 26<sup>th</sup> minute, where the value reached 5000 units in 10 ml of N-hexane,
- Heptadecanal was recorded at the 28<sup>th</sup> minute, where its value reached the highest value of up to 450,000 units in a solution of 10 ml of N-hexane.

All these values were measured in 4 out of 5 measurements, where the color of the chromatogram distinguishes the individual measurements. Black represents the first measurement, blue represents the second measurement, red represents the third measurement, green represents the fourth measurement, and yellow represents the fifth measurement.

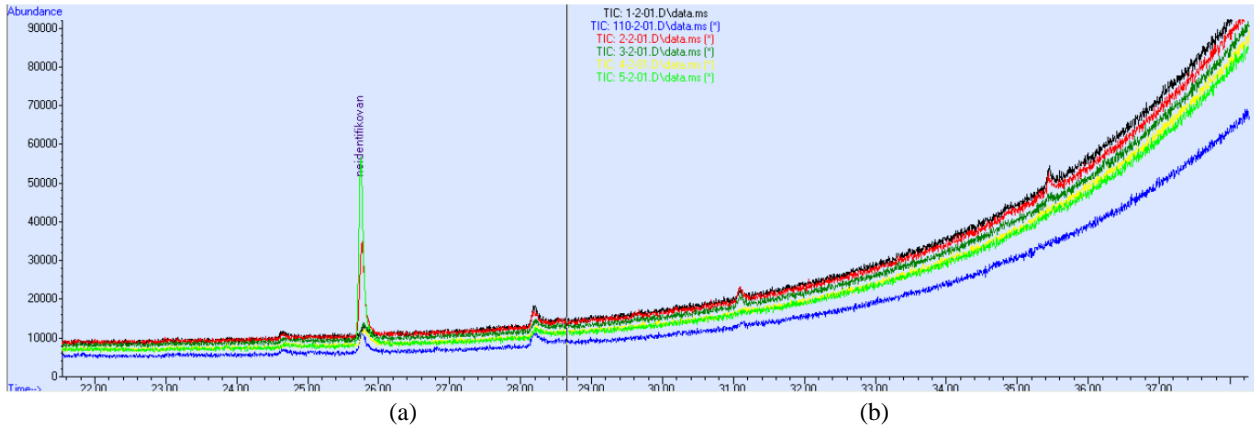


Fig. 12. Chromatogram - unwashed clothes, middle jacket pocket (source: elaborated by authors)

The mentioned chromatogram shows that on the unwashed clothes, specifically in the middle pocket of the jacket, where the samples were placed, an unidentified substance was recorded in 26 minutes, reaching 6000 units in 10 ml of N-hexane (Figure 12).

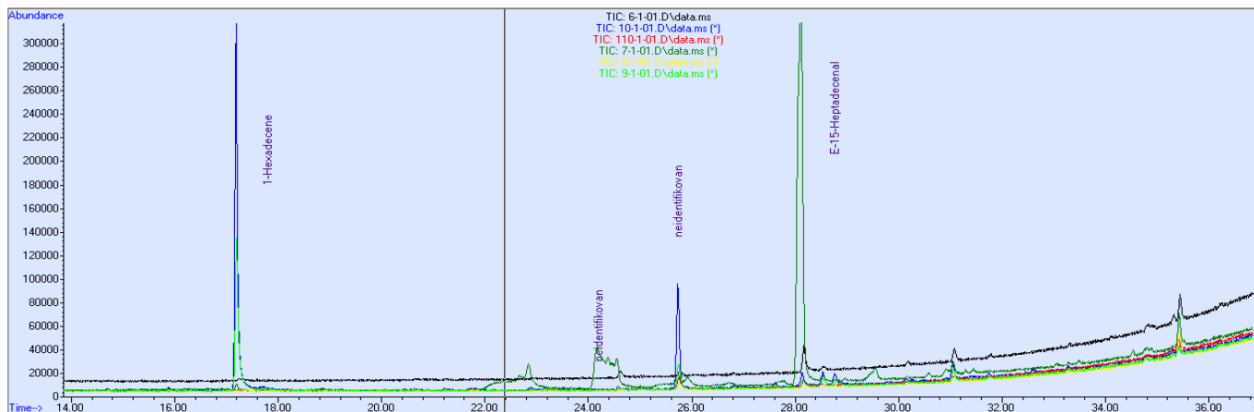


Fig. 13. Chromatogram - washed clothes, chest (source: elaborated by authors)

It follows from the mentioned chromatogram (Figure 13) that the following substances were measured on the washed clothes, specifically on the chest where the samples were placed:

- 1-Hexadecene was recorded at the 17<sup>th</sup> minute, where the value reached 40,000 units in 10 ml of N-hexane,
- Peridentified was recorded at the 24<sup>th</sup> minute, where the value reached 40,000 units in 10 ml of N-hexane,
- An unidentified substance was recorded at the 26<sup>th</sup> minute, where the value reached 10000 units in 10 ml of N-hexane,
- E-15 Heptadecanal was recorded at the 28<sup>th</sup> minute, where its value reached 40000 units in a solution of 10 ml of N-hexane.

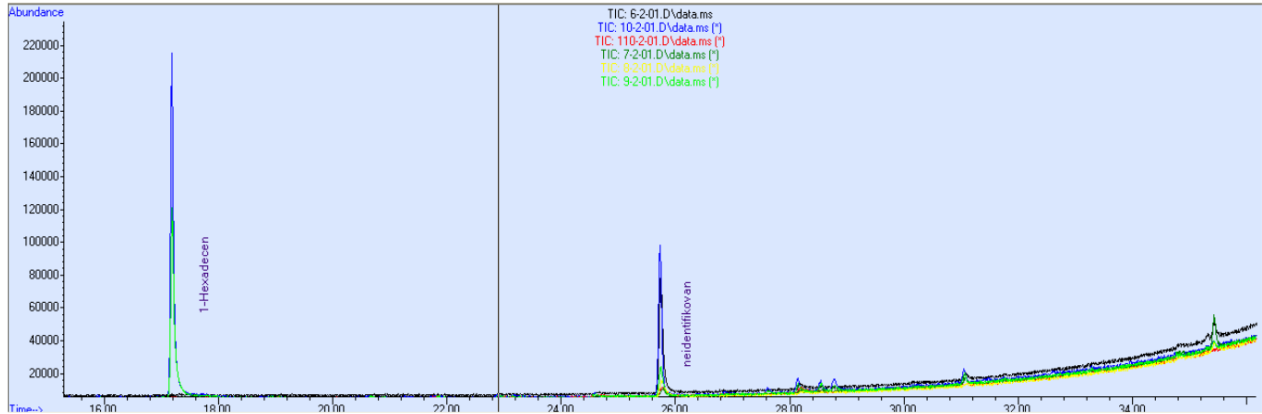


Fig. 14. Chromatogram - washed clothes, middle jacket pocket (source: elaborated by authors)

It follows from the mentioned chromatogram that the following substances were measured on the washed clothes, specifically in the middle pocket of the jacket, where the samples were placed (Figure 14):

- Hexadecene was recorded in the 17<sup>th</sup> minute, where the value reached 22000 units in 10 ml of N-hexane,
- An unidentified substance was recorded at the 26<sup>th</sup> minute, where the value reached 10,000 units in 10 ml of N-hexane.

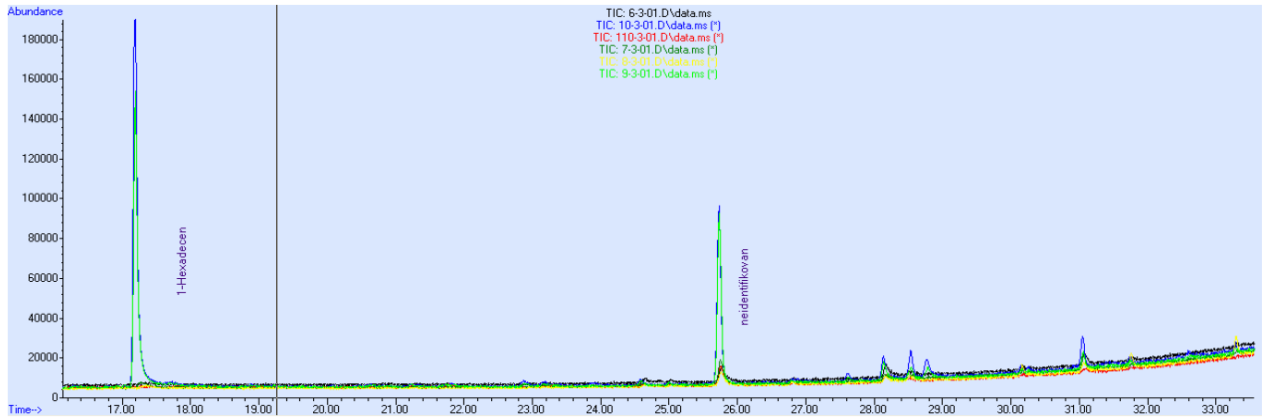


Fig. 15. Chromatogram - helmet (source: elaborated by authors)

The mentioned chromatogram shows that the following substances were measured in the helmet in which the sample was stored (Figure 15):

- Hexadecene was recorded at the 17<sup>th</sup> minute, where the value reached 2000 units in 10 ml of N-hexane,
- An unidentified substance was recorded at the 26<sup>th</sup> minute, where the value reached 10000 units in 10 ml of N-hexane. The substances found based on GC-MS are listed in Table 1.

All detected substances in the samples are listed in Table 1. These are substances that were found on the clothes before and after washing.

Tab. 1. Substances in samples (source: elaborated by authors)

Unwashed clothes	Washed clothes
Cyclohexane	1 - Hexadecene
Oxadecene	E-15 Heptadecenal
Cyclohexadecene	
E-14 Hexadecenal	
E-15 Heptadecenal	

The mentioned substances are used as solvents, are harmful to health, can cause death after use, and are irritating and poisonous. The mentioned substances are used as solvents, are harmful to health, can cause death after consumption, and are irritating and poisonous. As shown in Table 1, the listed substances are used as solvents, are harmful to health, can cause death after use, and are irritant and poisonous. If we compare the data from Table 1, E-15 Heptadecenal is also present in the samples before the actual washing and drying

process. It follows from the above that during fires in abandoned and demolished buildings, there may be substances that release these dangerous and health-damaging substances as a result of the fire.

### Discussion

The effects of toxic substances were characterized at the beginning of this work, where the exposure of firefighters at the scene of the intervention was confirmed by the research itself. In the chromatograms, individual dangerous substances were indicated to which the firefighters were exposed. The results themselves provided a picture of the danger to life and health caused by the effects of the mentioned substances, while it should be taken into account that the length of exposure, the effect of pressure differences in abandoned and demolition buildings, where the presence of openings reduces the effect of these substances on the responding firefighters, has a significant impact on the contamination process itself.

Substances that have been found during research, such as Cyclohexadecene, result in short-term exposure to reddening of the eyes and skin and in long-term exposure, which can be considered the case of firefighters, damage to the larynx and mucous membranes.

As for hexadecene substances, in this case, Acute exposure to hexadecane causes irritation, CNS depression, and gastrointestinal tract irritation. It may be fatal if swallowed and enters the airways; substances known to cause human aspiration toxicity hazards or to be regarded as if they cause human aspiration toxicity hazards.

As an illustration, the proven model can point to the Skellefteå model for inspiration to reduce these adverse effects and protect firefighters exposed to these risks (Figure 16) [Nomeir and Doina-Abou, 1985; Brandmån, 2015].

The listed measured concentrations of dangerous substances using GC, where long-term exposure can cause various damage to the health of firefighters. As was emphasized in the article, the conditions for the performance of the job are not the most suitable, and it is necessary to point out the necessity of changing certain regulations for the protection of life and health.

This model, which is a proposal for improving conditions, is a point system that illustrates and describes how firefighters can avoid hidden dangers in the course of their duties using simple routine operations and logical steps. The main goal is to avoid serious diseases due to long-term and repeated contact with dangerous and carcinogenic substances. The model is based on the basic thesis "from one intervention to another intervention". It summarizes the cyclical activity of firefighters during their service. [Nomeir and Doina-Abou, 1985; Brandmån, 2015].

The basis is that all equipment aimed at intervention is clean and free of toxic and dangerous substances. They belong here:

- Personal protective work equipment,
- Vehicle interior,
- Means for body protection,
- Means for respiratory protection,
- Material and technical equipment are located in the vehicle [Cavillo et al., 2019].

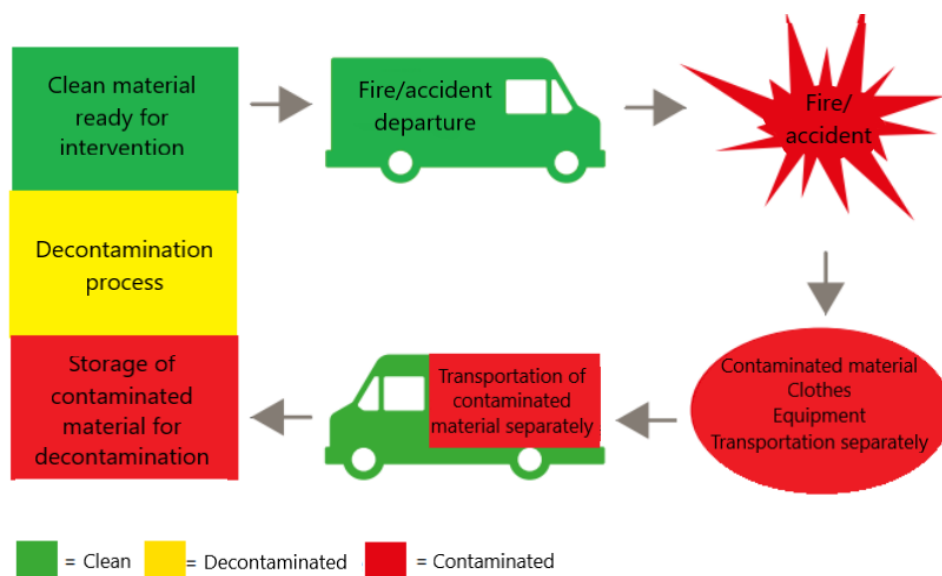


Fig. 16. Skellefteå model (source: elaborated by authors)

The leading solution to ensure maximum protection is to have a spare amount of emergency clothing on standby. The clothes should be in different sizes, which can be used as replacements in case of more interventions. In such situations, where members have to move from one place to another place in the area of an emergency. Similarly, as a replacement in such a case, if the decontamination of emergency clothing is already underway at the fire station.

These solutions must also be followed for breathing apparatus and all material and technical means used (bags, cases, packaging, special devices, etc.). In the case of more extensive and long-lasting interventions, it is necessary to prioritize means of transport such as trucks, ecological cars, buses, etc.

It is generally known that the working environment of firefighters and other emergency services is a complex problem. Despite the known risks, few documented plans exist to address the firefighter work environment. Based on the measured findings, it is necessary to state that for our purposes, it is necessary to make adequate decisions. For these decisions, a model such as Skellefteå appears to be an example of how the working environment of firefighters can be substantially improved without complicating the overall work process. The goal of the research is not to point to an existing model but as a possible way out.

It should be remembered that firefighters have never worked and will never work in an environment without the presence of dangerous substances. It's practically unreal. In addition to events dangerous to human health, there is a long chain of repeated and often unnoticed activities. That is when firefighters are most exposed to the effects of dangerous substances. This chain harms the rescue operation, so breaking it is necessary.

Although these agents have a natural ability to prevent the absorption of dangerous substances, the resistance of firefighting equipment to dangerous gaseous substances and aerosols needs to be clearly and precisely determined. These may contain particles (mechanical and other), especially in their working environment. Emergency clothing and equipment are designed primarily to protect against combustion products and flames. However, research has clarified that these combustion products and gases contain many toxic and dangerous substances. The emergency clothing is not primarily intended to prevent these particles from contacting the firefighter's skin. For this reason, it is also necessary to provide new, clean emergency clothing and equipment that did not come into contact with combustion products and those used during the intervention to be appropriately decontaminated and, if necessary, replaced with new ones after each intervention (Figure 17).



Fig. 17. The organization of individual zones (source: elaborated by authors)

## Conclusion

The goal was to find out what toxic substances remain in the emergency clothing of firefighters after an intervention. While the amount of dangerous substances released during a fire is enormously large, the research was narrowed down to polycyclic aromatic hydrocarbons, which are primarily characterized by their properties as carcinogenic.

The experimental measurement took place in an uninhabited and long-term abandoned building, in the building of the former East Slavic mills and bakery in Košice on the 2<sup>nd</sup> floor, in the administrative part of the building. A total of nine firefighters took part in the measurement. Each wore three fabric samples pinned to the inside of the garment (chest, center jacket, helmet). During the fire duration (over 2 hours), firefighters were exposed to smoke to the maximum extent possible. Then, half of the samples were taken immediately on the spot, and the other half were left on the garment until the garment was washed. All samples were subjected to GC-MS analysis in the Control Chemical Laboratory in Jasov.

There were six measured and recognized substances in the textile — four in the samples that were not washed and one in the samples that were washed. One substance (E 15 – Heptadecenal) was present in both cases, i.e., after intervention and after washing.

Several reasons exist for the small number of substances measured in the samples. One of the reasons may be the size of the used samples. Their location and dimensions may have needed to have been more optimal for capturing a sufficient amount of toxic substances. Another reason for the measurement result could be the laboratory method used. The amount of toxic substances in the samples may have been below the measurable limit of the measuring device. Finally, it is the length of exposure to smoke, where the fire was extinguished relatively quickly, and the type of building. It is common knowledge that long-abandoned buildings have many openings for fresh air supply and smoke removal outside the building. This results in low exposure limits for firefighters. It should be noted that, despite these low limits, there remains a problem with the working resources of firefighters, which must be solved unconditionally.

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