EFFECTIVENESS OF REMOVAL OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS DEPOSITED ON BREATHING APPARATUS BACK PLATES USED BY FIREFIGHTERS DURING FIRES

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Abstract

This paper presents the preliminary results of a study of the effectiveness of removing selected organic compounds emitted during a fire from firefighters' respiratory protective equipment. The research involved the determination of polycyclic aromatic hydrocarbons deposited on the back plates of the respiratory protection apparatus (pyrene, naphthalene, indeno[1,2,3-cd]pyrene, fluorene, phenanthrene, chrysene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[a]anthracene, acenaphthylene and acenaphthene) and to establish their removal efficiency in a process involving the use of a dedicated washer. Using liquid chromatography coupled to a diode array detector, compounds that were evolved in the fire environment and subsequently deposited on the surface of breathing apparatus back plates from different manufacturers were determined. Polycyclic aromatic hydrocarbons (PAHs) were determined before and after fire tests and after cleaning in a washer. As compared to the control samples, significantly higher PAH contents were recorded after testing in the fire chamber, which decreased several times after cleaning with a dedicated cleaner. Based on the results of the study, it was concluded that considering the lifetime of the equipment, carrying out a proper cleaning process of the equipment can significantly contribute to the minimisation of the exposure of firefighters to harmful compounds, resulting in the health of firefighters.

Keywords: fire environment, contaminant deposition, polycyclic aromatic hydrocarbons, respiratory protective equipment, contaminant removal

1. Introduction

In July 2022 the International Agency for Research on Cancer – IARC, an agency of the World Health Organisation (WHO) reassessed after 12 years the firefighters'

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occupational exposure to carcinogens. In 2010 IARC assigned firefighter exposure to group 2B – substances potentially carcinogenic to humans. In 2022, the classification was changed and firefighter exposure was assigned to group 1 – substances carcinogenic to humans (IARC, 2022).

Firefighters come into contact with a number of hazardous substances during their work. Their working environment is composed of contaminated air (containing, among other things, carbon monoxide, nitrogen oxides and aliphatic, cyclic and aromatic organic compounds). Numerous studies confirm the harmful effects of organic compounds on human health (Zhang et al., 2020; Soni et al., 2017; Liu et al., 2021). The presence of hydrocarbons in a firefighter's work environment and the identified carcinogenic properties (IARC, 2023) of some of them justify the exposure classification of firefighters developed by IARC.

Organic compounds can originate from a variety of sources (Yang et al., 2021; Yurdakul et al., 2017; Liu et al., 2019). They are formed during thermal decomposition and combustion of materials containing carbon in the structure (Majder-Łopatka et al., 2022). Their presence has been confirmed during fires (Peng et al., 2023; Austin et al., 2001; Fent et al., 2018; Fent et al., 2015; Porowski et al., 2018; Ömer et al., 2020). The group of organic compounds comprises polycyclic aromatic hydrocarbons (PAHs), of which benzo[a]pyrene is the most commonly determined. This compound is classified as a carcinogen and the carcinogenic and mutagenic activity of other polycyclic compounds is determined in relation to it (Table 1).

Table 1. Carcinogenic and mutagenic activity of selected PAHs

Name of compound	Carcinogenic activity	Mutagenic activity
Benzo[a]pyrene	1.0	1.0
Pyrene	0.081	0.20
Indeno[1,2,3-cd]pyrene	0.232	0.14
Chrysene	0.004	0.37
Benzo[k]fluoranthene	0.066	-
Benzo[ghi]perylene	0.022	0.08
Benzo[a]anthracene	0.145	0.62

Source: own study based on (Sapota, 2002)

In 2021, firefighters in Poland were dispatched to 579,722 interventions. More than 18% of these incidents (106,466) involved fires (Marzec, 2022; KG PSP, 2022). The number of fires in which involved the intervention of firefighters can be linked to their exposure to organic compounds. Aromatic hydrocarbons are deposited on the equipment used during rescue operations and on special clothing used by firefighters, after which they are transferred to fire stations (Rogula-Kozłowska, 2020). The ingress of toxic compounds can occur via inhalation, dermal absorption and ingestion. The causes of contamination comprise surface contamination, permeation, direct contamination and a secondary one (cross-contamination) (Fire Brigade Union, 2020). As a consequence a firefighter, despite being adequately protected with protective equipment (breathing apparatus and protective clothing) during and after operations, is exposed to toxic substances. Often, elevated levels of carcinogens are reported in firefighting units and fire vehicles (Łukawski, 2019). Exposure occurs as a result of offgassing of VOCs and during penetration of deposited hazardous substances, e.g. from protective equipment to the skin surfaces of the rescuer. Reducing secondary contamination and consequently minimising firefighter exposure can be achieved by using a correct and effective equipment decontamination process. Currently, no systematic procedures for cleaning equipment in Poland are available. Nevertheless, the provisions of binding law (Regulation of the Minister of Internal Affairs and Administration of 31 August 2021 on detailed conditions of occupational safety and hygiene for firefighters of the State Fire Service) indicate that a firefighter's personal protective equipment, in particular helmets, balaclavas and gloves, immobility alarms, torches, respiratory protection equipment and communication equipment need to be cleaned and disinfected. However, the regulation does not address the frequency of cleaning of equipment.

The Fire Service Occupational Cancer Alliance indicates that in the USA approximately 60% of retired firefighters suffer from various types of cancer (Fire Service Occupational Cancer Alliance, 2017). It is therefore important to reduce firefighters' exposure to carcinogenic compounds. For several years, cancer prevention has been discussed worldwide. Among firefighters, research is being conducted to identify exposure and exposure pathways. More and more standards, procedures and regulations are being introduced to ensure that firefighters' exposure to harmful agents is minimised.

In line with this trend, full-scale fire tests were conducted at the Fire Academy training ground between June 2021 and May 2022. The aim of the study was to establish the amount of carcinogenic compounds deposited on firefighters' respiratory protective equipment before and after the fire tests, and to determine the effectiveness of their removal through a wet cleaning process in a dedicated washer.

2. Research methodology

The research consisted in determining the content of selected polycyclic aromatic hydrocarbons deposited on the back plates of breathing apparatuses used during firefighting operations. Using high-performance liquid chromatography coupled to a diode array detector, the concentrations of: pyrene, naphthalene, indeno[1,2,3-cd]pyrene, fluorene, phenanthrene, chrysene, benzo[k]fluoranthene, benzo[ghi]perylene, benzo[b]fluoranthene, benzo[a]pyrene, benzo[a]anthracene, acenaphthylene and acenaphthene were determined. Measurements were taken with an HPLC 1260 Infinity liquid chromatograph integrated with a DAD diode array detector (Agilent Technologies Inc, USA). A C18-PAH, 3 μm, 150 mm x 2.0 mm column was used. Methanol and water were used as eluant. The measurement was performed at a flow rate of 0.35–0.45 cm^3/min and at 32°C.

Three types of back plates from air apparatus commonly used by firefighters in Europe were used in the study. Back plates No. 1 and 2 were from manufacturer A, while back plate No. 3 was made by manufacturer B (Figure 1).

Figure 1. Back plates of air breathing apparatus a) back plate No. 1 of producer A, b) back plate No. 2 of producer A, c) back plate No. 3 of producer B

The shoulder and waist belts and other components of manufacturer A's back plates are made of textile materials, while in the manufacturer's B back plate the presence of textile materials has been reduced to a minimum and most components are made of rubber (Figure 2).

Figure 2. Shoulder straps of breathing apparatus back plates a) back plate No. 1 of producer A, b) back plate No. 2 of producer A, c) back plate No. 3 of producer B

Nine back plates were used in the study – three of each type. The research was carried out in three stages. The test specimens were prepared in the same way in each stage. The slings were placed in a 60 dm^3 rectangular tank and flooded with

40 dm^3 of distilled water. After 24 hours, 1000 ml of liquid samples were collected and submitted to analysis. Water was used for the study, as it is a solvent commonly found in the firefighter's working environment. In the subsequent stages of the study, it is planned to use organic solvents to leach out contaminants.

In the first stage of the study, control tests were performed. The content of polycyclic aromatic hydrocarbons deposited on the back plates was determined prior to the contamination of the respiratory protective equipment (before entering the fire chamber). After the control test, the back plates were placed in a ventilated room until dry. The same back plates were used in the second stage of the study. At the Fire Academy's Field Training and Rescue Innovation Base, an internal fire was simulated in a modular trainer (Fig. 3.) containing a fire chamber.

Figure 3. Multi-module trainer with fire chamber

The fire chamber is a room with a volume of 78 m^3, at the end of which is a hearth. On the walls surrounding the hearth combustible material may be installed consisting of wooden pallets, extruded pallets and OSB boards.

In the study, six OSB boards were used to represent the fire conditions with dimensions of 1250×2500×18 mm. The boards were placed in dedicated locations on the wall and ceiling of the fire chamber, and a stack of offcuts created after cutting the boards was placed in the corner of the fire chamber (Figure 4). The fire chamber prepared in this way replicates the fire conditions and phenomena occurring during the real operations that firefighters undertake during internal fires.

Once the OSB combustion process had been initiated and the container has become fully smoke logged, firefighters were brought inside. During the fire test, nine firefighters equipped with personal protective equipment - breathing apparatus, special clothing, firefighter's hood, firefighter's helmet, combat gloves and combat boots - were inside the chamber (Figure 5).

Once inside the fire chamber, the firefighters performed typical elements of firefighting operations used during rescue operations, i.e.: they carried out a search of the rooms and administered water jets to the source of the fire and to the ceiling zone (Fig.6). The firefighters worked in full smoke for 20 minutes.

Figure 4. Fire chamber prepared for fire tests

Figure 5. Firefighters secured with PPE

Figure 6. Firefighting operations in a fire chamber

After leaving the fire chamber, the contaminated PPE was deposited on PP sheeting. Then cylinders, second stage regulators and full face masks were unscrewed from the breathing apparatus back plates. The back plates prepared in this way were placed in previously prepared containers and flooded with distilled water. After 24 hours, samples were taken and the PAH content was determined.

In stage three, the instrument back plates were placed in a specialised TopClean M washer (Meiko, Germany) for the cleaning process. The back plate cleaning process took 15 minutes. GT500 (Etolit, Germany), a product containing amines and alcohols, was used as the cleaning agent. After the washing process, the back plates were placed in containers and flooded with water, according to the previously described methodology. After 24 hours, samples were again taken and the previously determined PAHs were quantitatively analysed.

3. Results of studies and discussion

Using high-performance liquid chromatography integrated with a diode array detector, compounds were separated and PAHs quantified. Table 2 shows selected results.

Given the limitation of the method (measurement range), it was impossible to determine the exact content of some of the PAHs tested. It was found that in all samples taken before and after the fire tests, the concentration of: indeno[1,2,3-cd] pyrene, benzo[b]fluoranthene, benzo[ghi]perylene, benzo[k]fluoranthene was less than 0.0050 μg/l, while chrysene was less than 0.050 μg/l.

Based on the results, the sum of PAHs (Figure 7) and the multiplicity of the increase in PAH content after the fire tests relative to the control sample were calculated (Table 3).

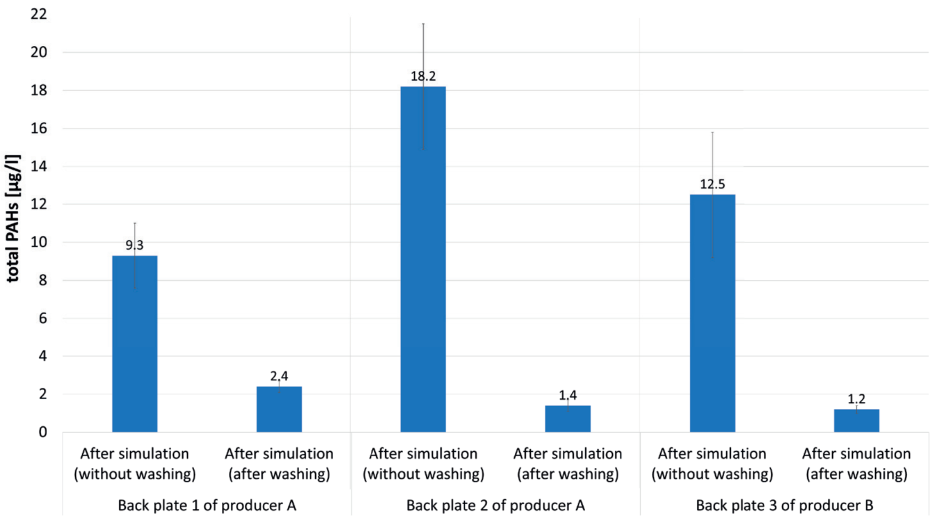
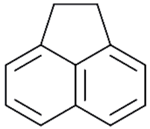
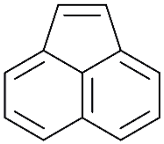
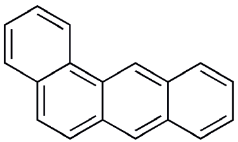
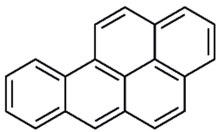
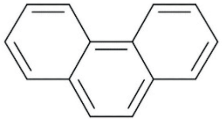
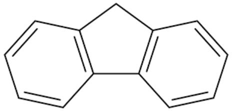
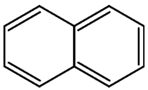
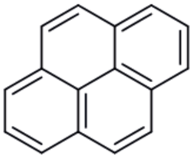


Figure 7. Total PAHs determined after fire tests and after cleaning in a dedicated washer

Table 2. Selected results from the determination of polycyclic aromatic hydrocarbons

		Back plate No. 1 of producer A		Back plate No. 2 of producer A		Back plate No. 3 of producer B	
		concentration [µg/l]	m.u.*	concentration [µg/l]	m.u.*	concentration [µg/l]	m.u.*
Acenaphthen 	Before fire tests	< 0.050	-	< 0.050	-	< 0.050	-
	After fire tests	> 0.50	-	> 0.50	-	> 0.50	-
	after washing	> 0.50	-	> 0.50	-	0.42	+/-0.06
Acenaphthylene 	Before fire tests	< 0.050	-	< 0.050	-	< 0.050	-
	After fire tests	0.2	+/-0.03	0.32	-	0.29	+/-0.03
	after washing	< 0.050	-	< 0.050	-	< 0.050	-
Benzo[a]anthracene 	Before fire tests	< 0.005	-	< 0.005	-	0.0064	+/-0.0009
	After fire tests	0.068	+/-0.010	0.057	+/-0.008	0.082	+/-0.010
	after washing	0.012	-	< 0.005	-	0.012	+/-0.002
Benzo[a]pyrene 	Before fire tests	< 0.002	-	< 0.002	-	0.0029	+/-0.0005
	After fire tests	0.003	+/-0.0005	0.0031	+/-0.0006	0.0041	+/-0.0006
	after washing	< 0.002	-	< 0.0020	-	< 0.002	-

Phenanthrene 	Before fire tests	< 0.005	-	< 0.0050	-	< 0.005	-
	After fire tests	> 0.50	-	> 0.50	-	> 0.50	-
	after washing	0.26	-	0.19	+/-0.03	0.26	+/-0.04
Fluorene 	Before fire tests	0.0072	+/-0.001	< 0.005	-	0.016	+/-0.002
	After fire tests	> 0.50	-	> 0.50	-	> 0.50	-
	after washing	0.25	-	0.1	+/-0.01	0.093	+/-0.013
Naphtalene 	Before fire tests	< 0.050	-	< 0.050	-	< 0.050	-
	After fire tests	> 0.50	-	> 0.50	-	> 0.50	
	after washing	> 0.50	-	0.48	+/-0.05	0.28	+/-0.03
Pyrene 	Before fire tests	< 0.005	-	< 0.005	-	0.0081	+/-0.0014
	After fire tests	0.13	+/-0.02	0.13	+/-0.02	0.14	
	after washing	0.03	-	0.017	+/-0.003	0.026	+/-0.004

m.u.* – measurement uncertainty

Table 3. Multiplicity of increase in content of selected PAHs after fire tests compared to control sample

	Back plate No. 1 of producer A	**Back plate No. 2 of producer A**	**Back plate No. 3 of producer B**
Sum of PAHs (from calculation)	1291.67	> 3640.00	378.79
Acenaphthen	> 10.00	> 10.00	> 10.00
Acenaphthylene	> 4.0	> 6.4	> 5.8
Benzo[a]antracene	> 13.6	> 11.4	12.81
Benzo[a]pyrene	> 1.5	> 1.55	1.41
Fenantren	> 100.00	> 100.00	> 100.00
Fluorene	> 69.44	> 100.00	> 31.25
Naphtalene	> 10.00	> 10.00	> 10.00
Pyrene	> 26.00	> 26.00	17.28

The sum of PAHs on the firefighter's personal protective equipment was found to increase significantly compared to the control sample after the fire tests. In the cases of a back plate made primarily of rubber material, an increase of more than 370 times was ascertained. Larger increases were found for back plates made of textile materials. An increase of almost 1,300-fold was found in tests of manufacturer A's back plate No. 1, while an increase of more than 3,600-fold was recorded for manufacturer A's back plate No. 2. Taking this into account, further research should be carried out to indicate whether it is reasonable to develop recommendations for the materials of which the breathing apparatus back plates should be made.

A review of data in the table shows that already after a 20-minute stay in the fire compartment, a significant amount of hydrocarbons, including carcinogenic and potentially carcinogenic substances, were deposited on respiratory protective equipment. For individual hydrocarbons, increases ranging from a few dozen per cent to even more than 100 times have been recorded. For the carcinogenic compound benzo[a]pyrene, an increase of between 40% and 55% was observed after fire tests. In contrast, for the possibly carcinogenic compounds (according to IARC) benzo[a]anthracene and naphthalene, an increase in concentration of more than 10 times was found in all tests. Depositions of PAHs on firefighters' personal protective equipment are also confirmed by the results of other studies. A report produced by Stull indicated that benzo[a]anthracene, chrysene, fluoranthene, phenanthrene and pyrene were identified on the clothing of firefighters (Technical Report, International Personnel Protection, Inc., 2006). In a study by Kirk and Logan (2015) on organic compound deposition, pyrene, benzo[a] anthracene, phenanthrene have been detected on the outer layer of a firefighter's protective clothing in all fabric samples. The possibility of secondary emissions of PAHs in the working environment of firefighters has been identified (Rogula-Kozłowska, 2020). Elevated hydrocarbon concentrations have been reported in fire stations (Rakowska et al., 2022). Studies indicate that in rooms where personal protective equipment is stored PAH concentrations in the atmosphere tend to be higher (Rogula-Kozłowska et al., 2023; Banks et al., 2021).

Studies have confirmed that there are hazardous substances on the respiratory protective equipment with which every firefighter comes into contact not only during operations, but also afterwards, contains hazardous substances. As air cylinders need to be replaced following every action, the study focused on the air breathing apparatus back plates.

The back plates used during the tests initially contained only trace amounts of the hydrocarbons tested (total PAHs < 0.05 μg/l). Tests carried out after the fire tests showed significantly higher amounts of these compounds on the surface of the air apparatus back plates. Considering the harmfulness of the determined compounds, it is reasonable to take measures to reduce the possibility of secondary contamination.

The removal methods of deposited contaminants currently used in Poland usually consist of manual washing of air apparatus back plates. This activity is not performed after each introduction of the equipment into the fire environment. The back plates are cleaned several times per year, by different people and in different ways. Research indicates that this form of cleaning is ineffective (Stec et al., 2018). The study established the effectiveness of the back plate cleaning process after the use of a washer and an amine and alcohol-based cleaner. The study was designed to find whether the back plate cleaning process could be automated, shortened and, at the same time, significantly reduced the level of contamination. The parameter E was used to establish the efficiency of the PAH removal process, which was determined from the formula:

$$E[\%] = \frac{C_p - C_m}{C_p} \cdot 100\%$$

E [%] – pollutant removal efficiency,
C_p – concentration of test compound after fire simulation (without washing),
C_m – concentration of test compound after fire simulation (after washing).

It was assumed that a satisfactory result was to achieve for total PAHs a removal efficiency > 70% and a reduction in the concentration of the carcinogenic compound benzo[a]pyrene in the test samples below 0.0020 μg/l.

The PAH removal efficiency of a 15-minute automatic back plate cleaning in a dedicated washer is shown in Table 4.

Table 4. Removal efficiency of selected PAHs

[%]	Back plate No. 1 of producer A	Back plate No. 2 of producer A	Back plate No. 3 of producer B
Sum of PAHs (from calculation)	74.19	92.31	90.40
Acenaphthen	> 1.00	> 1.00	> 16.00
Acenaphthylene	> 75.00	> 84.37	> 82.75
Benzo[a]antracene	82.35	> 91.22	85.37
Benzo[a]pyrene	33.33	35.48	> 51.21
Fenantren	> 48.00	> 62.00	> 48.00
Fluorene	> 50.00	> 80.00	> 81.40
Naphtalene	> 1.00	> 4.00	> 44.00
Pyrene	76.92	86.92	8143

After cleaning in a dedicated washer, the value of total PAHs did not exceed 2.5 µg/l, and for two types of back plate the value was less than 1.5 µg/l (Figure 7). The removal efficiency of the PAH sum was higher than 70%. In the case of 2 back plate types, it was found to exceed 90%. There was a significant reduction in the concentration of carcinogenic and potentially carcinogenic substances: benzo[a] pyrene and benzo[a]anthracene (Figure 8) and naphthalene.

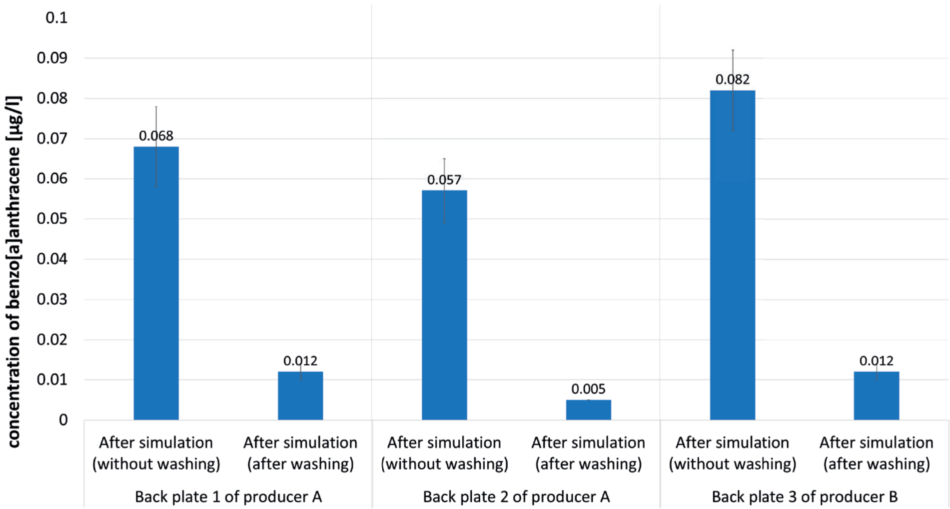


Figure 8. Benzo[a]anthracene concentration measured after fire tests and after cleaning in a dedicated washer

After the cleaning process, benzo[a]pyrene concentrations were found to be lower than 0.0020 µg/l in all the tested samples. The removal efficiency of the carcinogenic benzo[a]pyrene was more than 30% and of the potentially carcinogenic benzo[a]anthracene more than 80%.

It was found that the type of material from which the air apparatus back plate is made influences the deposition and removal process. The total amount of contaminants deposited on a back plate made of rubber was several times lower than for those made of textile materials. In addition, some substances such as naphthalene or acenaphthene were more difficult to remove from the material surface under test conditions.

4. Conclusions

An analysis of obtained results allows making the following assumptions:

1. The use of dedicated washers and appropriate agents can automate and shorten the cleaning process of breathing apparatus back plates while ensuring high PAH removal efficiency.
2. Using a 15-minute cleaning process can significantly reduce the amount of contaminants deposited on the back plates. In the studies carried out, the removal efficiency of total PAHs was high, ranging from 74% to over 92% depending on the types of back plate.
3. The cleaning process in a dedicated washer ensures the reduction of the carcinogenic compound benzo[a]pyrene deposited on the surface of the back plate.
4. The effectiveness of PAH removal depends on the material of the back plate. It has been found that in removing some compounds, e.g. naphthalene from textile surfaces is more difficult than from rubber surfaces.
5. Carrying out a proper and thorough cleaning process for equipment used in firefighting operations can have a significant impact, considering the lifetime of the equipment, on minimising the exposure of firefighters to harmful compounds, resulting in the health of firefighters.

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EFEKTYWNOŚĆ USUWANIA WYBRANYCH WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH ZDEPONOWANYCH NA NOSZAKACH APARATÓW POWIETRZNYCH STOSOWANYCH PRZEZ STRAŻAKÓW PODCZAS POŻARÓW

Abstrakt

W artykule przedstawiono wstępne wyniki badań efektywności usuwania ze sprzętu ochrony dróg oddechowych strażaków wybranych związków organicznych wydzielających się podczas pożaru. Badania polegały na oznaczeniu zdeponowanych na noszakach aparatów ochrony dróg oddechowych wielopierścieniowych węglowodorów aromatycznych (pirenu, naftalenu, indeno(1,2,3-cd) pirenu, fluorenu, fenantrenu, chryzenu, benzo[k]fluorantenu, benzo[ghi]perylenu, benzo[b] fluorantenu, benzo[a]pirenu, benzo[a]antracenu, acenaftylenu oraz acenaftenu) oraz określeniu efektywności ich usuwania w procesie prowadzonym z wykorzystaniem dedykowanej myjki. Przy wykorzystaniu chromatografii cieczowej sprzężonej z detektorem diodowym oznaczono związki, które wydzieliły się w środowisku pożarowym, a następnie osadziły się na powierzchni noszaków aparatów powietrznych różnych producentów. Oznaczono wielopierścieniowe węglowodory aromatyczne (WWA) przed i po testach pożarowych oraz po czyszczeniu w myjce. W porównaniu do prób kontrolnych, po testach w komorze ogniowej, odnotowano istotnie wyższe zawartości WWA, które kilkukrotnie zmalały po przeprowadzeniu czyszczenia z wykorzystaniem dedykowanej do tego procesu myjki. Na podstawie wyników badań stwierdzono, że przeprowadzanie właściwego procesu czyszczenia sprzętu może znacząco wpłynąć, biorąc pod uwagę okres użytkowania sprzętu, na minimalizację narażenia strażaków na szkodliwe związki, co w efekcie przekłada się na zdrowie strażaków.

Słowa kluczowe: środowisko pożarowe, depozycja zanieczyszczeń, wielopierścieniowe węglowodory aromatyczne, sprzęt ochrony układu oddechowego, usuwanie zanieczyszczeń