Toxicity of Combustion Products from Fires

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Abstract: - Firefighters, as well as victims, can be exposed to various toxic products of combustion generated during a fire. Therefore, this paper deals with certain chemical constituents of smoke from burning widespread materials, the toxicity of common hazardous chemicals, and potential health effects on firefighters and affected population from exposure to the fire smoke. Furthermore, firefighter gear can be polluted by toxic products during operations and it may cause further contamination of the fire station interior. The purpose of this paper is to consider exposure in firefighters.

Key-Words: - combustion products, exposure, fire, health effects, toxicity, firefighters

1 Introduction

This paper is intended to present primary outcomes in connection with doctoral project, which is dedicated to long-term monitoring of toxic substances released from fires and potential health effects on firefighters. The aim of the project is to identify toxic substances generated during fires and determine concentrations of selected substances in order to assess potential impact on the health of firefighters, who do not wear respirators. The second objective is to consider whether the fire station interior is moreover contaminated by toxic combustion products. According to this goal, the project deals with the identification of combustion products released from repeatedly contaminated firefighter gear, which is stored in locker room in fire station after incidents. It is believed, that firefighters are potentially exposed to toxic substances deposited in fire station interior. Following step is to consider chronic exposure in firefighters in such conditions. The project addresses need for missing procedures in Fire Rescue Services in the Czech Republic for treatment of firefighter gear. Moreover, the spectrum of the most frequent combustion products is not specified.

2 Analysis of Current State

In respect of health effects arising from fires, it could be said that most of casualties suffer from acute and chronic exposure to toxic substances more than from burns [1]. Therefore, this part focuses mainly on the adverse health effects particularly to firefighters exposed to the toxic products in fire smoke.

Although conditions of burning will be different for each fire, several commonalities can be found. The combustion products generated during fire can differ depending upon the material involved. However, general assumptions about the hazardous chemical constituents most likely present in fire effluent can be made if the material is known.

The hazardous products formed during combustion of major organic products can be divided into two following basic categories in terms of their toxicity: asphyxiants and irritants. Furthermore, there could be a third category of such products which have other toxic effects. The third category may typically include complex molecules with longer carbon chains or carbon rings [1].

The amount and chemical properties of hazardous products formed during combustion depend on fuel type and other specific circumstances related to the dynamic nature of fire. Several commonalities about the most important toxic products can be recognized on the basis of the material known.

Firefighters health risks resulted from fires are mostly connected with specific materials used nowadays. Current consumption has resulted in widespread application of polymeric materials, rubber, wood, hazardous chemicals, oil and other specific materials. The following paragraphs deal with chosen chemical components of fire smoke formed during combustion of specific materials.

ISBN: 978-1-61804-139-5

2.1 Toxic Combustion Products Formed by Material Involved

Synthetic materials such as plastics, foams and resins have massive utilization, particularly in many common household items. Therefore, they may be subject of combustion and produce toxic products when burned under specific conditions.

The combustion of polyurethane (PUR) yields the formation of CO under most combustion conditions. Very low oxygen concentrations can support generation of HCN [2]. The combustion of polyurethane foams generally applied in furnishing and other PUR products can form isocyanates and their derivates, aromatic compounds as benzene and toluene [1, 3]. The combustion of other polymers which also contain nitrogen such as nylons and polyacrylonitriles (PAN) produces considerable amounts of NOx and ammonia. In laboratory conditions, it was estimated that 1.5 up to 15 g of HCN may release from 1 kg of PAN [4].

The gaseous products from pyrolysis of polyethylene (PE) with very low oxygen concentrations can be methane, ethane and hydrogen. Under conditions of incomplete combustion with 38 % of carbon included, 13.4 % of CO, 42.6 % of volatile hydrocarbons (methane, ethylene, acetylene, toluene, benzene) and 5.3 % of PAHs were produced during PE pyrolysis [5].

Many polymeric materials used nowadays contain a significant amount of halogens and they are widely used in residents and buildings where many people can be exposed to the toxic products if these materials burn. The greatest hazardous combustion products of polyvinyl chloride (PVC) are hydrogen chloride (HCl) and chlorine (Cl). The combustion of 1 kg of PVC liberates approximately 400 l of gaseous HCl [6]. In addition, some chlorinated plastics can also release phosgene ($COCl_2$), small quantities of PCDDs and PCDFs. Other halogen plastics burned may generate hydrogen florid (HF) and hydrogen bromide (HBr). Fluorine containing polymers, e.g. polytetrafluoroethylene (PTFE) upon combustion liberates perfluoroisobutene (PFIB), which is more toxic than phosgene and it is an extreme irritant.

Rubber fires are nowadays represented by serious tire fires. During tire fires, significant amounts of many toxic products may be produced. Carbon oxides and soot particles are general combustion products from tire fires. Considerable concentrations of SO_2 and sulphur derivates are formed due to the sulphur content as a consequence of the vulcanization process. In experiments, emissions from car tire fires were assessed. Inorganic gases, volatile organic compounds (VOC), PAHs, PCDD, PCDF, PM and some metals were measured in fire smoke. [7] Characteristic combustion products are represented by 1,3-butadiene, styrene, 4-vinylcyclohexene and limonene. The combustion of rubber which contains organophosphates is also likely to form phosphorous pentoxide (P_4O_{10}) [1, 8].

Currently, there are possible fire hazards connected with usage and storage of different kinds of wood. Pollutants in emissions from uncontaminated and contaminated wood fires represent some of the toxic combustion products with adverse health effects. Burning of cellulose, such as in forest fires, leads to formation of organic irritants, such as acrolein, formaldehyde, simple and aromatic hydrocarbons [1]. Combustion of wood which contains natural essential oils and inorganic compounds, e.g. adhesives (PF or UF resins) and preservatives (heavy metals treatment), may yield liberation of PAHs, PM, polychlorinated biphenyls (PCBs), PCDDs, PCDFs, and small amounts of heavy metals as oxides [9].

2.2 Toxicity of Emphasized Combustion Products

Most common toxic combustion products formed during burning such materials mentioned above can be asphyxiant gases, e.g. carbon monoxide (CO), carbon dioxide (CO_2), hydrogen cyanide (HCN), irritant gases, e.g. nitrogen oxides (NO_x), sulfur dioxide (SO_2), halogen acids, organic irritants such as acrolein and formaldehyde, other inorganic irritants, e.g. ammonia (NH_3), phosgene ($COCl_2$), and complex molecules such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), isocyanates and particulate matters (PM).

The health hazard of generated toxic compounds is expected to be the greatest for such victims, particularly for firefighters, directly exposed to the smoke plume and outside the immediate vicinity of the fire source (e.g. incident commander). The emphasized combustion products in this paper are PAHs and PCBs.

PAHs are recognized as complex molecules with a minimum of two fused benzene rings. There is very poor information including adverse health effects resulting from acute exposure to PAHs. On the contrary, there are many studies that provide evidence about potential carcinogenic and mutagenic effects. Benzo[a]pyrene, naphtalene, chrysene and benzo[b]fluoranthene are the most common representatives of this large group of organic compounds. The International Agency for Research on Cancer (IARC) classifies benzo[a]pyrene as carcinogenic to humans (Group 1), naphthalene, chrysene and benzo[b]fluoranthene are possibly carcinogenic to humans as (Group 2B) [10]. US EPA categorizes benzo[a]pyrene, chrysene and benzo[b]fluoranthene as Group B2 as probable human carcinogen [11]. PAHs are primarily generated during combustion and are present in particles in ambient air. In the urban areas, the concentration of benzo[a]pyrene has been detected at the level of 0.6 ng/m^3, whereas in rural areas it is 0.3 ng/m^3 [12]. On the contrary, occupational exposures to benzo[a]pyrene by inhalation can be as high as 100 $\mu g/m^3$ [13]. Only one study [14] has been conducted in order to report some respiratory effects from chronic exposure to benzo[a]pyrene in occupational settings.

PCBs belong to group of chlorinated hydrocarbons. Due to their unique properties PCBs were used in industrial and commercial applications (e.g. as plasticizers paints, plastics, rubber products etc.) PCBs are able to cause cancer (Group 2A) as well as a variety of other adverse health effects on the immune system, reproductive system, nervous system, and endocrine system [15, 16].

3 Applied Methods and Devices

Based on compiled literature search, it can be believed that firefighters are exposed to many chemical substances with adverse health effects. It is assumed that these pollutants get stuck to firefighter gear and it probably contaminates the indoor environment which can finally result in further exposure of firefighters. For that reason our aim is to observe pollutant emissions and assess health risks continuously to support this premise.

Primary monitoring of combustion products released from contaminated firefighters gear left in interior after the actions has been initiated. The samples were collected with portable sampling device – continual aerosol concentrator [17].

The concentrator operates on the basis of accumulation of gases, vapours and aerosols in generated polydisperse aerosol of a suitable liquid. 660 μl/min of n-heptane was used as absorption liquid. The airflow rate was 400 ml/min.

The first step was to determine validity of the concentrator. The technique of collecting samples was verified using the denuder method. Detection limits of both used devices were identical.

Samples were collected using the concentrator in the interior of the fire station after three various fires in a given period of time. The first fire took place in an unused warehouse of a printing office, the second one happened in a warehouse without hazardous substances, and the last fire was residential fire in Brno. Samples were collected at 10 monitored places, especially at the room for used firefighter gear, store of used firefighter equipment, decontamination room and fire truck interior. In this paper, outcomes from only one analysis are presented.

The analysis of samples was conducted with method of gas chromatography-mass spectrometry (GC-MS) under specific conditions. The volume of air samples injected to the 30 m long column was 4 μl, the temperature in injector was 260 °C. The inner diameter of column was 0.32 mm with the stationary phase of 1 μm. The flow of carrier gas (helium) through the column was 4 ml/min. The analysis has run 54 min with 50 °C/2 min program; the temperature was increased by 5 °C/min up to 300 °C. The detection was carried out by MS with m/z in range of 20 – 550.

Simultaneously, passive samplers realized as 5 cm long tubes with 5 mm in inner diameter containing 0.2 g of TENAX were tested inside the simulator (closed shipping container – 70 m^3), where 250 kg of used wood pallets were burned. The container is used for training firefighters and enables simulation of a backdraft – an explosion of gaseous products generated during incomplete combustion in enclosed areas. The duration of fighting the fire was approximately 15 min. The extraction of collected substances was made by 3 ml of hexane-dichlormethan. The extract detection was carried out under similar conditions, except the volume of air injected to the column was 1 ml, the temperature gradient was 10 °C/min and m/z was 20 – 650.

4 Problem Solution

The GC-MS analysis was particularly focused on PAHs, PCBs and dioxins due to their adverse health effects resulted from their toxicity. Repeated acute episodes may eventually lead to chronic health problems [10]. Thus, there is potential hazard for active firefighters.

Although, presence of emphasized organic compounds in analyzed samples was not confirmed, the Sample 3 collected in interior of fire truck has been shown to contain 3,7,11,15-tetramethyl-2-hexadecen-1-ol (first peak), which is added to foam extinguishers as detergent.

Fig. 1 Continual aerosol concentrator – peak identification (Sample 3 - chromatogram)

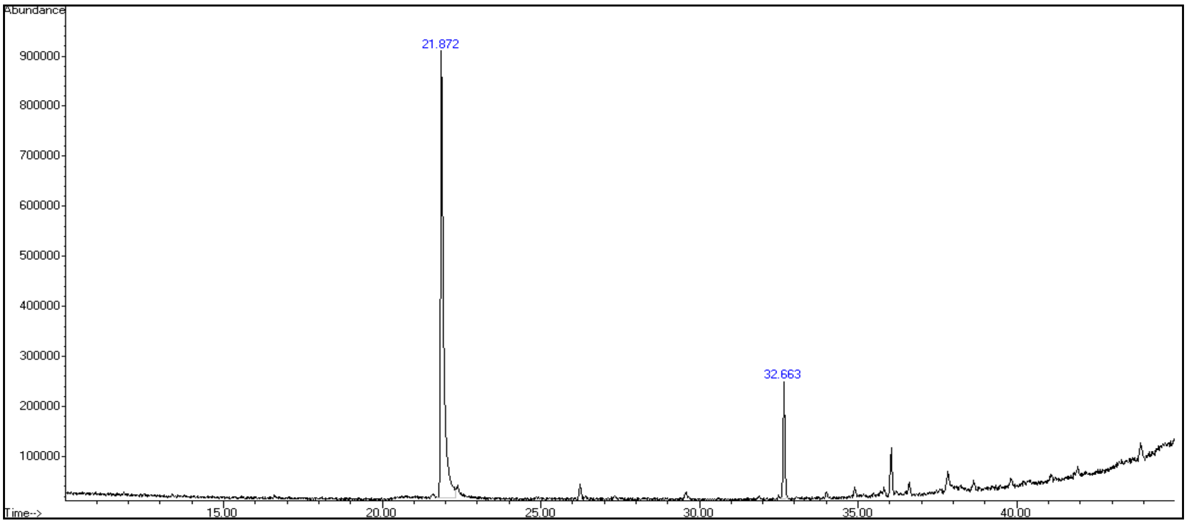
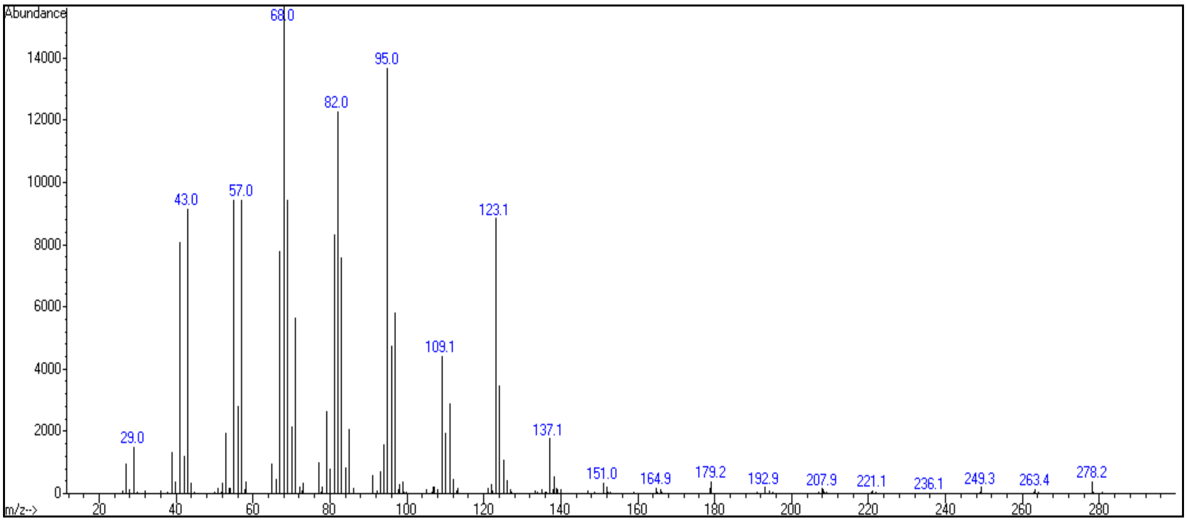


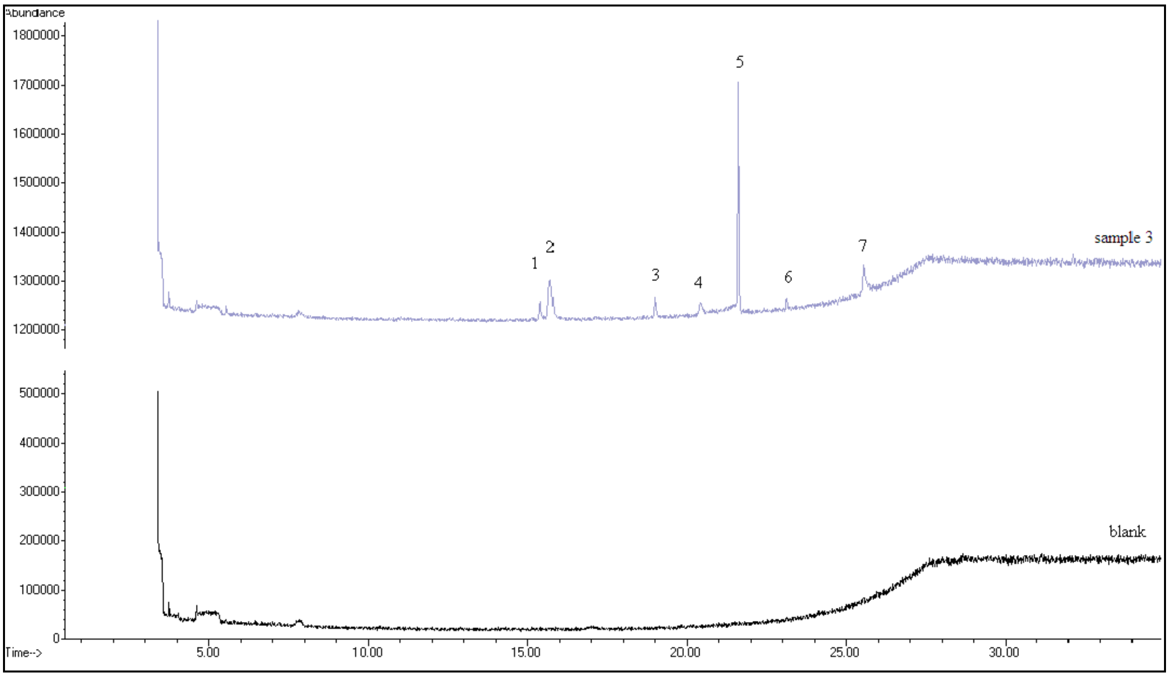
Fig. 2 Continual aerosol concentrator – peak identification (mass spectrum)



Absence of accented compounds can be explained by materials involved. Since the monitoring has been initiated, only three fires have occurred in selected locality, in which no significant amounts of hazardous substances were present. Figures above represent results from GC-MS analysis. First figure shows chromatogram of the Sample 3, which illustrates the identification of peaks and second one demonstrates mass spectrum.

Outcomes from analysis of samples collected by passive samplers used in the simulator show, that not only common gases, such as CO, methane, aldehydes and ketones collected by mobile device DRÄGER, were detected. GC-MS analysis of extract from 5 passive samplers indicates similar spectrum of chemical substances for each sample. The figure 3 illustrates results from GC-MS analysis of the Sample 3. The first peak corresponds with 2,4-bis(1,1-dimethylethyl)-phenol (58.2% probability), the second peak points to sulfur with 96.5% probability, the third peak was not identified, the peak no. 4 indicates diphenyl sulfone with 94.5% probability, the fifth peak is cyclic octaatomic sulfur with 98.7% probability, the peak no. 6 was identified as 2,6-diphenylphenol (29.7% probability) and finally the last peak was recognized as diisooctyl phthalate with 38.8% probability. The accented PAHs and PCBs were not identified. Therefore, it can be assumed that the continual aerosol concentrator have to be applied during these simulation as well. Furthermore, some modifications of passive samplers are desired due to longer diffuse trajectory of harmful substances. The exposition duration has to be also extended.

Fig. 3 Passive samplers – peak identification (Sample 3 – chromatogram)



4 Conclusion

Emissions from fires represent significant health and environmental hazard. Firefighters are exposed to several toxic combustion products with potential adverse health effects. Characteristics of the products result from specific conditions, especially from the material involved.

The project is realized in two ways. On the one hand, there is monitoring of the internal environment of the fire station and collecting samples by the continual aerosol concentrator. On the other hand, passive samplers with adsorbent are used to monitor external and internal environment of the simulator to achieve cumulative results about exposition of those who do not wear the respirator.

Although, presence of accented PAHs and PCBs in collected samples was not confirmed, it is necessary to monitor firefighter internal environment continuously. Therefore, the aim of subsequent efforts in this area will concentrate on the continual monitoring of the fire station interior, and health risks as a result of possible chronic exposure to toxic products released from repeatedly contaminated firefighter gear.

The analysis of extracts from passive samplers has not confirmed presence of emphasized toxic products of combustion. However, the monitoring in the simulator used by firefighters will continue. Passive samplers will be modified.

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ISBN: 978-1-61804-139-5