Flame Retardants in the City of Johannesburg EMS fire fighters bunker gear

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**Abstract**. Firefighting protective garment (bunker gear) is the main shield that firefighters use for protection against heat, flame and other hazards during fires. The bunker gear’s thermal protection is enhanced by the addition of flame retardants, which resist ignition and or reduces the rate of fire spread. Five (5) new and three (3) used bunker gears were investigated. Initial investigation of the bunker gear used by the City of Johannesburg EMS firefighters is found to contain brominated flame retardants, most of which have been found to be harmful to human and the environment and have been banned or restricted in most parts of the world. X-ray fluorescence (XRF) scanning measurements showed that all the samples contained significant amount of brominated flame retardants ranging from 4915 to 462 ppm. Comparison of the old (used in firefighting events) and new samples showed no significant difference in brominated flame retardant content. The fire retardants effects of the samples were investigated using the Cone Calorimeter under 50 and 75 kW.m-2 external heat fluxes. Heat release rate, smoke release rate and fire spread measurements on the samples showed low values attributed to the retardants in the bunker gear. The average fire growth rate index (FIGRA) for the samples were found to be 1.88 ± 0.44 kW.s-1 (5 new bunker gears) and 2.63 ± 0.37 kW.s-1 (3 old/used bunker gears) for external irradiation flux of 50 kW.m-2. FIGRA values for external heat flux 75 kW.m-2 were 5.07 ± 1.12 kW.s-1 and 6.17 ± 0.99 kW.s-1 for new and old respectively. In the case of smoke growth rate (SMOGRA), values found were 3.12 ± 0.34 and 4.96 ± 0.59 m2.s-2, respectively for new and used gears under 50 kW.m-2 irradiation and 13.26 ± 3.63 and 14.60 ± 2.37 m2.s-2 under 75 kW.m-2 heat fluxes.

1. Introduction

Firefighters make use of personal protective equipment and clothing when performing firefighting and other similar activities. Firefighter’s protective clothing provides shield and act as the first line of protection against flames, heat, smoke, steam and hazardous chemicals mostly encountered during firefighting [1,2]. Firefighter protective clothing comprises coat and trouser (bunker gear), helmet, safety boots, gloves, hood and safety googles. However, most of the thermal protection is offered by the bunker gear. Heat transfer in fire conditions through the firefighter’s clothing is largely due to radiant energy [3]. Bunker gear comprises three separate layers: an outer shell (outer layer), a thermal liner (middle layer) and a moisture barrier (inner layer). The outer shell provides a tough, durable first line of defence against heat, flame and abrasion [4,5,6]. The thermal liner provides insulation against heat penetration encountered during firefighting while the moisture barrier prevents water and other fire-ground liquids from entering the gear, keeping the thermal liner dry and ultimately the firefighter’s body protected from these outside elements [7,8,6].

To meet safety standards, firefighter garments are tested and certified according to the minimum requirements of the National Fire Protection Agency (NFPA) 1971 standard. The NFPA 1971 (2013 edition) specifies the minimum design, testing, performance, and certification requirement. In order to meet the minimum prescribed requirements and achieve superior thermal performance, firefighting protective garments are constructed from flame retardant fabrics. Flame retardant fabrics are achieved by adding flame retardant chemicals and or using inherent flame retardant fibres. Flame retardants are specifically designed to reduce or halt the spread of fire, allowing the exposed people to escape without harm. With higher retardant efficiency and lower decomposing temperature, brominated flame retardants (BFR), have become more popular as flame retardants than their halogen counterparts [9]. However, recently, BFRs have received considerable attention due to their toxicity to human and the environment. Some BFRs were identified as persistent, bio-accumulative, and toxic to both humans and the environment and were suspected of causing neurobehavioral effects and endocrine disruption [10]. The most economical and convenient route of introducing flame retardants is by mixing and blending them with the fabric/polymer, a process which could lead to leaching out the retandants into the environment [9].

Noting the possible hazards to human and the environment, however, some BFRs were listed under the Restriction of Hazardous Substances Directive (RoHS) as a "restricted substance" group (polybrominated biphenyls) in 2003 [10], and the Stockholm Convention (polybrominated diphenyl ethers - PBDE) in 2009 [11]. Despite the restrictions of some BFRs by most countries, there are growing concerns that some of the bunker gears used in the City of Johannesburg Fire Services may still contain some of these chemicals and their congeners. Furthermore, recent findings show that significant concentrations of BFRs (PBDEs specifically) are found in personal protective clothing worn in contact with the skin [12].

The present study seeks to analyse the material composition and thermal properties of the firefighting bunker gear and to understand the performance of flame retardants when exposed to fire conditions. The main objectives of this research were to analyse the material composition of structural firefighting bunker used in the City of Johannesburg EMS, identify and quantify BFRs, specifically PBDEs and their congeners in the garment, evaluate the thermal performance and combustion behaviour of bunker gear fabric.

1. Materials and methods

2.1. Garment and Chemical composition

Firefighting garment bromine (Br) content was measured using the Delta handheld XRF. Sample analysis was performed under Restriction of Hazardous Materials and Waste Electrical and Electronic Equipment Directive (RoHS/WEEE) mode and the analytical time was set at 30 s.

2.2. Thermal performance analysis

A cone calorimeter supplied by Fire Testing Technology Limited (FTT) was used for testing of the samples following ISO 5660-1 standard (Part1: Heat Release Rate). According to ISO 5660, the samples were cut to 100×100 mm2 sizes and placed over a heavy duty aluminium foil with a size 120×120 mm2 with the shining part facing the sample. The foil was then folded on the edges to cover the sample edges and the corners. The prepared sample was then placed over ceramic fibre back packing and put inside a square metal sample holder. A sample retaining wire grid was used to hold the sample in place to avoid the suctioning of the sample or foil by the hood during measurements.

Tests were conducted to measure the time to ignition (TTI), heat release rate (HRR) and smoke production rate (SPR) and other derived parameters such as Fire Growth Index Rate (FIGRA). The lower the FIGRA rating, the lower is the burn hazard from a given fabric once it is ignited [13].

Two different predetermined heat fluxes, 50 kW.m-2 and 75 kW.m-2, were used for taking measurements. For each sample type, experimental measurements were repeated three times at 50 kW.m-2 heat flux and twice at 75 kW.m-2 heat flux.

1. Results and discussion

Figure 1 represents a typical HRR profile of one of the samples. The peak heat release rate (PHRR) and the corresponding time value give the so-called Fire Growth Rate (FIGRA). Low FIGRA values as in Table1 are attributed to the efficacy of flame retardants used in the garments.

|  |  |  |
| --- | --- | --- |
| |  | | --- | |  | | **Figure 1.** Typical Heat Release Rate profile | |

Figure 2 shows a typical smoke production rate profile of a sample. The peak smoke production rate (PSPR) and the time it takes to reach gives the smoke growth rate index (SMOGRA).

|  |
| --- |
|  |
| **Figure 2.** Typical Smoke Production Rate profile |

Figure 3 shows the HRR versus time profiles of all the eight different PPE samples when subjected to external heat flux of 50 kWm-2. The old and used PPE (H and G but not F) have higher PHRR values as compared to the new ones. This evidence could be attributed to the weakening effect of the fire retardant chemical due to age, fabric washing procedure as well as previous heat exposure in firefighting activities. Time to ignition (TTI) for ‘used’ samples G and H could be seen as short as compared to the new PPE such as A and E.

|  |
| --- |
|  |
| **Figure 3.** Heat Release Rate profiles of samples when subjected to 50 kWm-2 |

The XRF results in this study presented a direct link between the bromine content and the middle layer of the firefighter protective clothing. The outer shell which is constructed to be tough and durable in order to resist abrasions and cuts provided the least bromine content in most samples. Surprisingly, the only outer shell that contained high bromine content was from the used protective garment. The results depicted a trend of high bromine content in the middle layer, thermal liner, which is designed to offer superior insulation against heat. Low bromine content was recorded on the inner layer which serves to provide moisture barrier. The US Environmental Protection Agency (US EPA) prescribes a maximum of 1000 *ppm* for PBDEs that can be contained in a material [9].

The summary of XRF measured bromine content together with the cone calorimeter results of the eight bunker gear samples are shown in Table 1. Samples A, B, C, D and E are new garments, while F, G and H are old/used garments. The results show that 63% of the samples have bromine content in excess of 1000 *ppm*. Among the new samples, measured BFR values for A, B and E are way above the maximum (1000 *ppm*) permissible by standards. Two of the three used ones have well above maximum BRF values. The expected general inverse relationship between the BFR content and the PHRR, high of the latter should give low of the former, was not seen in the samples. The possible reason could be the inclusion of other retardants that lie outside the BRF focus of the present study. However, sample **A** (new)took longest time to ignite(TTI = 28 s); had the highest BRF measured value (3457 *ppm*); showed the lowest PHRR of 63.6 kW.m-2 whilst sample **G** (used) with the lowest BRF value of 445 *ppm*, showed the highest PHRR of 166.2 kW.m-2. The FIGRA value of sample **A**, as expected, is relatively low (1.7 kW. m-2.s-1) for the 50 kW.m-2 external irradiation and that of **G** very high (3.5 kW. m-2.s-1) with TTI only 15 s. Smoke growth rate index (SMOGRA) seems to be associated to samples with higher BFR.

**Table 1.** XRF and Cone Calorimeter results

|  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Sample** | **BFR**  (ppm) | **TTI**  (s)  -50  kW. m-2 | **PHRR**  (kW.m-2) | | **PSPR**  (m2.s-1) | | **FIGRA**  (kW. m-2.s-1) | | **SMOGRA**  (m2.s-2) | |
| 50  kW.m-2 | 75 kW.m-2 | 50 kW.m-2 | 75  kW.m-2 | 50 kW.m-2 | 75  kW.m-2 | 50 kW.m-2 | 75 kW.m-2 |
| **A** | 3457 | 28 | 63.6 | 106 | 0.01 | 0.04 | 1.7 | 3.9 | 4.8 | 11.7 |
| **B** | 1730 | 24 | 93.4 | 142.3 | 0.02 | 0.04 | 2.1 | 4.7 | 4.0 | 14.3 |
| **C** | 462 | 12 | 80.1 | 145 | 0.01 | 0.03 | 1.5 | 6.1 | 1.2 | 14.6 |
| **D** | 478 | 26 | 82.5 | 128.9 | 0.01 | 0.04 | 2.1 | 6.4 | 2.8 | 16.0 |
| **E** | 2455 | 30 | 82.5 | 114.8 | 0.01 | 0.02 | 2.1 | 4.2 | 2.8 | 9.7 |
| **F** | 2961 | 29 | 79.6 | 123.5 | 0.01 | 0.04 | 1.6 | 4.0 | 3.1 | 13.2 |
| **G** | 445 | 15 | 166.2 | 276 | 0.03 | 0.05 | 3.5 | 8.5 | 5.2 | 16.9 |
| **H** | 4915 | 9 | 145.9 | 222 | 0.03 | 0.05 | 2.8 | 6.0 | 6.5 | 13.7 |

The average FIGRA for the 5 new bunker gears were found to be 1.88 ± 0.44 kW.s-1 and 2.63 ± 0.37 kW.s-1 (3 old/used bunker gears) for external irradiation flux of 50 kW.m-2. FIGRA values for external heat flux 75 kW.m-2 were 5.07 ± 1.12 kW.s-1 and 6.17 ± 0.99 kW.s-1 for new and old respectively. Similarly, SMOGRA values found were 3.12 ± 0.34 and 4.96 ± 0.59 m2.s-2, respectively for new and used gears under 50 kW.m-2 irradiation and 13.26 ± 3.63 and 14.60 ± 2.37 m2.s-2 under 75 kW.m-2 fluxes.

1. Conclusion

Firefighter protective clothing was analysed for BFR content and related thermal performance. The bunker gears were found to have PBDE content in excess of maximum permissible (1000 ppm). The efficacy of the BRF in the bunker gears, seen in the HRR and TTI as well as FIGRA and SMOGRA values was significant but varied in the eight samples studied. Further analysis and quantification of the brominated flame retardants (PBDEs) in the samples using gas chromatography-mass spectroscopy (GC-MS) is ongoing.

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