FLAME RETARDANT TEXTILE FINISHING CHEMICALS: IN VITRO ASSESSMENT OF DERMAL ABSORPTION

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ABSTRACT

Flame Retardants (FR) are a group of anthropogenic environmental contaminants used in textile finishings. Currently, the largest marked group of FRs is brominated FR considered toxic, persistent and bioaccumulative. Non-halogenated alternatives are a possible solution, but there is a lack of knowledge concerning environmental impact and health risks.

The aim is focused on dermal absorption of FR. Until now, no studies were found about the textile release of FR to the skin in contact with them. The evidence that dermal absorption could be potentially significant pathway of human exposure to FRs, supports the interest in the study.

Key Words: flame retardants, percutaneous absorption, HPLC- UV, sulfamate ammonium, cotton, polyester

1. INTRODUCTION

FRs are widely used in everyday consumer products including carpets, electronic appliances, clothing and textiles. Since 1970, polybrominated diphenyl ethers (PBDEs) have been widely used in consumer products as FRs. Several human health effects are associated with PBDEs exposure such as disruption of the endocrine and thyroid homeostasis. The commercial mixtures Penta-BDE and Octa-BDE have been described as persistent organic pollutants for elimination under the Stockholm Convention, while Deca-BDE mixture is under reviewer (Kademoglou et al., 2017) [1].

In Europe, Regulation EC 1907/2006 for Registration, Evaluation, Authorization and Restriction of Chemicals (REACH), was adopted to improve the protection of human health and the environment from the risks that can be posed by chemicals, while enhancing the competitiveness of the EU chemicals industry. REACH places the responsibility on industry to manage the risks that chemicals may pose to the health and the environment.

Some technological alternatives already exist on the marked, such as permanent FR free from formaldehyde based on polycarboxylated compounds, and permanent FR free from halogenated compounds and antimony (III) based on phosphorous and nitrogenized compounds.

LIFE-FLAREX is a project with the aim of contribute to the mitigation of the environmental and health impacts caused by toxic compounds resulting from bromide-, formaldehyde- and antimony- containing FR textile finishing products on European ecosystems, by analyzing the best available textile finishing products and implementing those innovative technologies for FR applications.

The project will demonstrate that the alternative FR products are economically and environmentally viable and do not represent a concerning health risk to humans or animals.

This LIFE Environmental Policy and Governance project, groups four textile clusters from Spain, Italy and Czech Republic (AEI TÈXTILS, ATEVAL, CLUTEX and CS-POINTEX) which represent the industrial textile sector of their countries and also, joins two technological centers from Spain and Belgium (LEITAT and CENTEXBEL) and a Spanish research center (IQAC) that belongs to the Spanish Research Council (CSIC). The innovation cluster "AEI TÈXTILS" is the Leader of the Project.

The preliminary work of the LIFE-FLAREX project has been focused on the selection of the most representative textile materials and finishing technologies normally used in the textile sector.

Some home textiles, such as bedclothes or pajamas, are in contact with skin for long periods, while people sleeping. In the present study, an action of LIFE-FLAREX project, the aim is focused on dermal absorption of FR. Until now, no studies were found about the textile release of FR to the skin in contact with them. The growing evidence that suggests dermal absorption to be potentially significant pathway of human exposure to FRs, supports the interest in the study of percutaneous absorption of the FR.

The first absorption percutaneous experiments have been done with cotton and polyester fabrics containing flame retardants based on nitrogenized compounds, in concrete, sulfamate ammonium, with the aim of determine the amount of active substance that may cross the stratum corneum and to enter into deeper skin layers.

2. EXPERIMENTAL PART

Two commercial FR were used applied onto different fabrics. Both have as active principle ammonium sulfamate. In Table 1 there are the products and fabrics used.

Table 1. Flame retardants based on ammonium sulfamate used and textile fabrics treated

FR code	Composition	Textile code	Description
FR A	Ammonium sulfamate <50%	**Flarex004-047**	PES/CO 50/50 mattress ticking treated (pick-up 11 wt%) with FR A
		Flarex004-035	PES mattress ticking treated (pick-up 13 wt%) with FR A
FR B	5-15% (1-Hydroxy-ethilene) bisphosphonic acid	**Flarex002-2/CO**	CO bed linen treated (pick-up 10 wt%) with FR B
	5-15% urea		
	5-15% Ammonium sulfonate		
	<0.25% Phosphorous acid		
	<0.2% acetic acid		

The textile treatment was done at CENTEXBEL (Ghent).

Before the percutaneous absorption assays of FR finished textiles, two preliminary tests have been considered in this work:

- Test at time 0h (recovery from the skin surface). A 10 µL solution of the tested substance has been applied on the skin surface fitted in a diffusion cell thermostated at 32ºC and immediately that substance has been extracted with a solvent and analyzed.
- Blank tests of the skin compartments. From acceptable and non used previously pig skin preparations, the different compartments have been isolated (SC, Epidermis and Dermis) using conventional procedures. 10 µL of the tested substance has been

applied on each skin compartment and the exposure time has been maintained at 32ºC for 24 hours. The compounds were extracted with a solvent and analyzed.

Also, the recovery of the tested substance in receptor fluid was carried out applying 10 µL of the tested substance in a given volume (3 mL) being subsequently analyzed an aliquot of the receptor fluid.

The individual recoveries of the tested substance from each skin compartment, skin surface and receptor fluid must be nearly complete if a validated analytical methodology and a suitable extraction process have been used. The recovery should be within the range 100 ± 15%.

Another previous assay was the ammonium sulfamate quantification in each FR product and on each treated textile fabric. A piece of each textile (2 x 2 cm^2) was extracted and analysed by HPLC-DAD.

For percutaneous absorption studies, pig skin was used with a thickness of approximately 500 ± 50 µm. Skin discs with a 2.5cm inner diameter were prepared and fitted into static Franz-type diffusion cells.

A control skin disc (without product application on the skin surface) was used to rule out possible interferences in the analysis by HPLC-DAD. According to the OECD methodology [2], the skin penetration studies were performed for 24 h of close contact between the textile and the skin. To increase the contact pressure between the textile fabric and skin, permeation experiments were carried out by placing a steel cylinder on the textile-skin substrate at a constant pressure in accordance with standard conditions (125 g/cm^2) (ISO 105-E04, 1996) (see Figure 1).

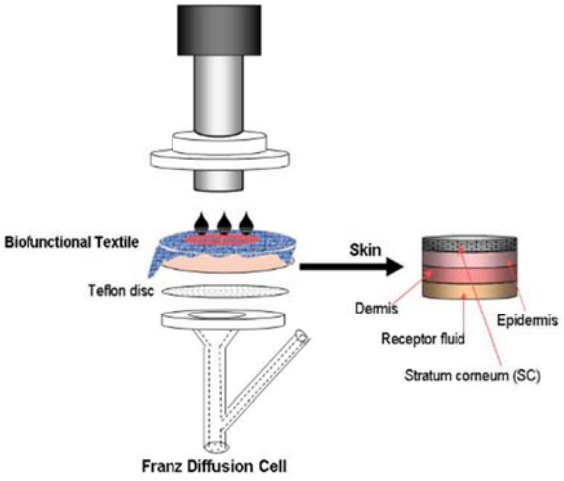


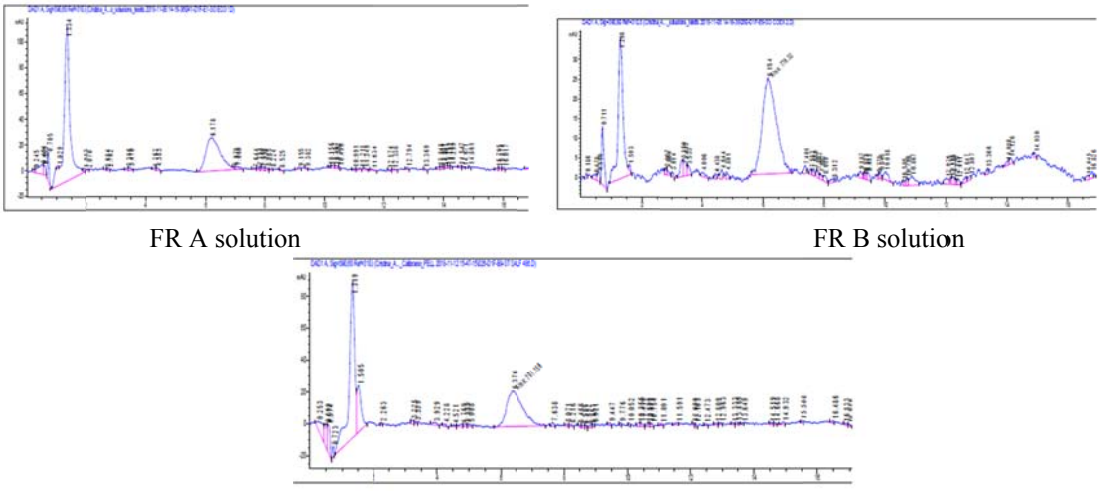
Figure 1. Diagram of *in vitro* percutaneous absorption experiments.

After the exposure time, the receptor fluid was collected, the fabrics were removed from the skin surface and collected together with the top of the cell. The stratum corneum of the skin was removed using adhesive. The epidermis was separated from the dermis after heating the skin [3].

All samples were analysed by HPLC using a PRP-X100 column (Hamilton, 10 µm, 150x4.6 mm) using a mobile phase of p-hydroxybenzoic acid (5.8 mM, pH 9.4)/ methanol at isocratic conditions of 3%methanol. The sample volume injected was 40 µL and the flow was 1,5 mL/min. The detection was made with diode array detection (DAD) obtaining a signal at 310nm [4].

4. RESULTS AND DISCUSSION

Preliminary tests demonstrated that ammonium sulfamate was detected without interferences from skin or textile. Then, HPLC-DAD methodology was validated with a LOD (detection limit) of 2.051 µg/ml and LOQ (quantification limit) of 6.215µg/ml. Then, the quantification of FR products and the treated textiles were done (Figure 2 and Table 2).



FR A solution FR B solution

Ammonium sulfamate standard

Figure 2. HPLC-DAD Chromatograms obtained for each FR, and for ammonium sulfamate standard

Table 2. Concentration of ammonium sulfamate in each FR formulation, and amount of ammonium sulfamate on each treated sample

SAMPLE	% Conc (w/w)	µg /mg textile
FR A	40.03±2.51	-
FR B	37.19±0.36	-
Flarex002-2(CO)	-	75,77±16.5
Flarex004-035 (PES)	-	145,04±15.2
Flarex004-047 (PES/CO)	-	111,29 ±6.4

FR A presented a concentration of 40% in accordance with the commercial specification formulation. However a higher sulfamate concentration for FR B, 37.19%, was found.

After first tests, the treated textiles were used to perform the percutaneous absorption following the scheme in Figure 1. The results obtained are detailed at Table 3 and plotted in Figure 3.

Table 3. In vitro percutaneous absorption of ammonium sulfamate from treated textiles. (T: rest on fabric, SC: stratum corneum; E: epidermis; D: dermis; FR. receptor fluid: R: scrap).

%	2_FR B	035_FR A	047_FR A
T	93,82±6.12	79,94±8.10	66,54±4.15
SC	1,08±0.32	0,44±0.13	0,73±0.68
E	0,63±0.13	0,06±0.11	0,00
D	<LOQ	<LOQ	<LOQ
FR	<LOQ	<LOQ	<LOQ
R	15,79±1.47	5,75±10.20	16,61±2.47
TOTAL	111,32±5.98	86,19±5.22	83,88±4.49
Perc.Abs.	0,63±0.13	0,06±0.11	0,00

The major part is retained on the textile (66-94%) and smaller amount (0.44-1.08%) is passed to the SC.
The percutaneous absorption is considered as the sum of E, D and FR, in our study, two samples, one with FR B and other with FR A, presented a slight penetration into the first layer epidermis. The percutaneous absorption of the FR active compound in two samples could be due to the type of textile or to the FR formulation.

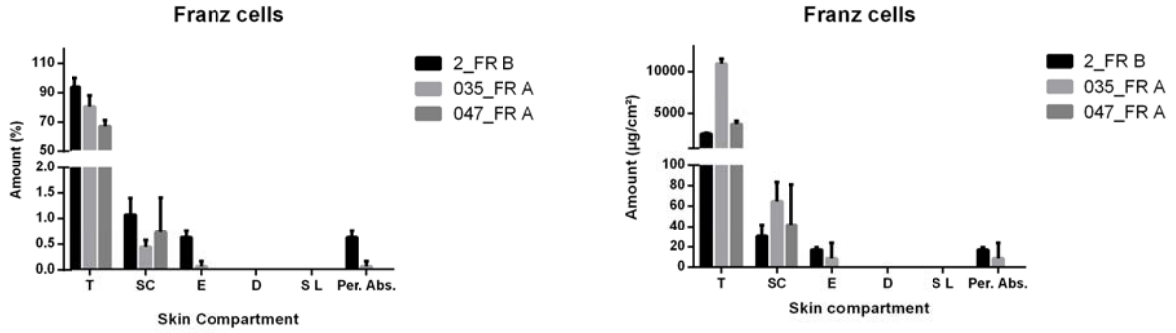


Figure 3. Percutaneous absorption from the treated textile samples with two different FR based on ammonium sulfamate, expressed into % of ammonium sulfamate and µg ammomium sulfamate per cm^2 of fabric. (T: rest on fabric, SC: stratum corneum; E: epidermis; D: dermis; FR. receptor fluid: R: scrap).

5. CONCLUSIONS

In this study, the possible topical dermal route for textile finishing products from fabric was demonstrated in the particular case of flame retardant product based on ammonium sulfamate. Three different fabrics (PES/CO, PES and CO) for two different final applications (mattress ticking and bed linen) were used with two different commercial flame retardant products, with the same active compound, ammonium sulfamate.

The percutaneous absorption experiments have been demonstrated that topical application of this textiles permit the active compound penetration until epidermis for both commercial products, for cotton with 15% of ammonium sulfamate (FR B) and for PES with 40% of

ammonium sulfamate (FR A). Although the percutaneous absorption has been very small, between 0.06% and 0.63% of ammonium sulfamate applied on the textiles.

The final aim of this study is the risk characterization of the different alternative flame retardant products for finishing textile industry, so the amount of FR substance that cross the stratum corneum and enter into deeper skin layers is important to calculate the Margin of Safety (MoS) of each active compound.

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