An Analytical Method for Alternative Flame Retardants in Chairs and Car Seats to Evaluate Direct Dermal Exposure from Interior Consumer Products

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Introduction

Flame retardants (FRs) were included in interior consumer products to reduce a risk of fire hazard. Hexabromocyclododecane (HBCD), which is classified as one of brominated flame retardants (BFRs), had been widely used before the Stockholm Convention on Persistent Organic Pollutants restricted the use and the manufacture due to its environmental risks. As alternatives to HBCD, phosphorus flame retardants (PFRs) have been proposed [1-4]. However, some PFRs have adverse health effects to human. Tris(2-chloroethyl) phosphate (TCEP) exhibits neuro- and reproductive toxicity [5]. Tris(1,3-dichloropropyl) phosphate (TDCPP) is suspected to be a human carcinogen [6]. Therefore, there are concerns about the risks of PFRs for human health.

PFRs in interior consumer products are supposed to be taken to human via two typical exposure routes, inhalation and dust ingestion [7]. In addition to them, the dermal exposure has recently started to attract attentions as an alternative exposure route for PFRs. According to a previous study [8], chemicals which have certain molecule weight (<500 g/mol) can penetrate through the skin, and this penetration cannot be efficiently reduced by clothes on the skin. Given that chairs are likely to be in contact with the skin for a long time and with a large contact area, the dermal exposure of PFRs via direct contact with chairs must be one of the most important exposure route as with the inhalation and dust ingestion.

To calculate the dermal exposure rate via direct contact with interior consumer products such as chairs, the information on the concentrations of PFRs in them is required. However, the analytical method to measure PFRs in interior consumer products has not been established. In our previous study [9], we found that inadequate extraction methods (ultrasonication with inadequate extraction solvent) were not completely capable of extracting all the PFRs included in polyester curtains from the curtains. The concentrations of PFRs extracted by the inadequate method were 200 times less than those by the adequate extraction method. To accurately determine the concentrations of PFRs in interior consumer products, analytical methods should be optimized for each product, at least for each material constituting the products (e.g., polyester, polyvinyl chloride, polyurethane).

In this study, to develop an optimum analytical method for PFRs in chair and car seats, which are likely to be in contact with the skin for a long time, the effects of extraction methods on the concentrations of PFRs in the extracts were investigated.

Materials and methods

Samples

Interior consumer products targeted in this study were 2 kinds of car seat and 3 kinds of chair, which were classified and labelled according to category of products and their materials (fabric and urethane form). The

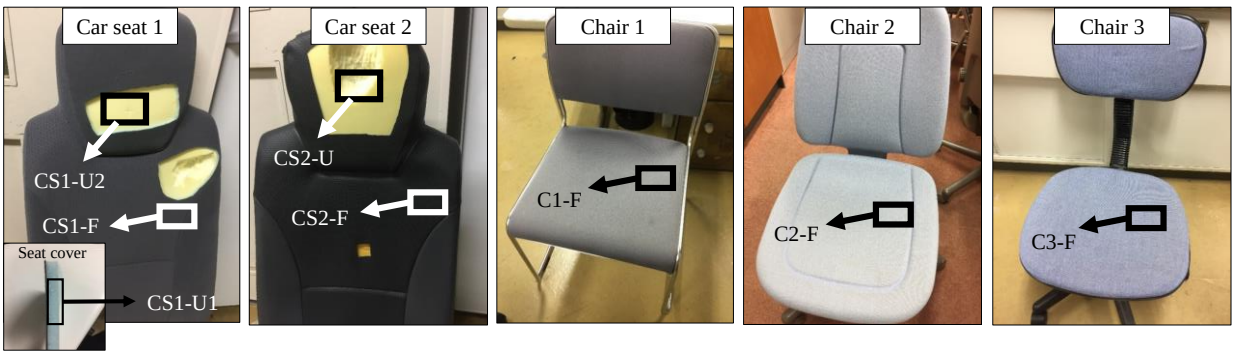

Figure 1: Samples of chairs and car seats and their sample IDs.

pictures of the samples and sample IDs are shown in Figure 1.

Extraction procedure

In our previous study [9], 25% 1,1,1,3,3,3-hexafluoro-2-propanol/chloroform (HFIP) and dichloromethane (DCM) showed great extraction rate for PFRs in polyester curtains. Therefore, in this study, HFIP and DCM were selected as extraction solvents. In addition to them, tetrahydrofuran (THF) was also selected. As extraction method, ultrasonication and Soxhlet extraction were used and compared.

For the ultrasonication, the chairs and the car seats were cut into small pieces (0.1 g) with respect to each material (fabric and urethane form). A 2 mL of extraction solvent were added into the sample in a test tube with clean-up spikes (tris(2-ethylhexyl) phosphate [TEHP]-d_{51}, triphenyl phosphate [TPhP]-d_{15}, tricresyl phosphate [TCsP]-d_{21}, and tris(2-chloroethyl) phosphate [TCEP]-d_{12}), and it was then extracted by the ultrasonication for 10 min. After adding an 8 mL of toluene, it was re-extracted by the ultrasonication for 10 min. Then, it was centrifuged at 3000 rpm for 10 min. A 10 µL aliquot of the supernatant was transferred to a vial, spiked with 20.0 µL tributyl phosphate (TBP)-d_{27} (1 µg/mL) as an internal standard, and diluted with acetonitrile to final volume of 1 mL.

For the Soxhlet extraction, the cut sample was put into an extraction thimble with the clean-up spikes. It was extracted by the Soxhlet extraction method with 250 mL of DCM for 16 h. Then, the extract was concentrated to 1 mL by an evaporator, and diluted with toluene to 10 mL. A 10 µL aliquot was transferred to a vial, spiked with 20.0 µL TBP-d_{27}, and diluted with acetonitrile to final volume of 1 mL.

Analytical procedure

Fifteen PFRs targeted in this study are as follow: trimethyl phosphate (TMP), triethyl phosphate (TEP), tripropyl phosphate (TPP), TBP, tris(isobutyl) phosphate (TIBP), TEHP, tris(butoxyethyl) phosphate (TBOEP), TPhP, cresyl diphenyl phosphate (CsDPhP), 2-ethylhexyl diphenyl phosphate (EHDPhP), TCsP, TCEP, tris(2-chloroisopropyl) phosphate (TCPP), TDCPP, and trisphenylphosphine oxide (TPhPO).

The concentration of the 15 PFR in the extracts were determined by using a liquid chromatograph interfaced with a triple quadrupole mass spectrometer (LC-MS/MS) (Thermo Fisher Scientific Inc.) in atmospheric pressure chemical ionization (APCI) mode. A 2 µL aliquot of the extract was injected onto a Accucore Vanquish C18 column (internal diameter: 2.1 mm, length: 100 mm, particle size: 1.5 µm) with water (Solvent A) and 20% acetonitrile/methanol (Solvent B) as the mobile phases at a flow rate of 300 µL/min. The column temperature was

maintained at 50°C. The gradient program was as follows: isocratic at 10% solvent B for 1.8 min, 10% to 80% solvent B in 0.2 min, isocratic at 80% solvent B for 2.0 min, 80% to 100% solvent B in 1.0 min, isocratic at 100% solvent B for 4.0 min, 100% to 10% solvent B in 0.5 min, and then isocratic at 10% solvent B for 3.5 min. The MS/MS are operated under selected reaction monitoring (SRM) mode.

Results and discussion

Effects of extraction methods on extraction rate

Our previous study found that the complete dissolution of sample was able to assure the complete extraction of targeted analytes from the sample owing to getting homogeneous solution [9]. Polyester (the samples of C1-F−C3-F) was able to be completely dissolved, while solid of polyurethane (the samples of CS1-U1, CS1-U2, and CS2-U) remained in the extracts after the extraction. Therefore, to investigate the effects of the extraction methods on the extraction rates, we measured the extraction rates for TCPP from polyurethane (CS1-U1) by the Soxhlet extraction with DCM, and the ultrasonications with DCM, HFIP, and THF. In this study, the relative extraction rate was used for the comparison of extraction efficiencies for the extraction methods tested in this study, because the true value of the concentrations of TCPP in CS1-U1 was unknown. The relative extraction rates were calculated as follows: the concentrations of TCPP extracted by each extraction method were divided by those extracted by the Soxhlet extraction with DCM. The results are shown in Figure 2. The highest relative extraction rate was obtained in the ultrasonication with THF (129%). On the other hand, the relative extraction rates of the ultrasonications with DCM and HFIP were 28% and 9.2%, respectively. The Soxhlet extraction method requires taking much time and a large variety of glasswares, and routinely checking the cross-contamination from high-concentration samples due to being indisposable apparatus [10]. Therefore, although the ultrasonications with inadequate extraction solvents are not preferred, the ultrasonication with the adequate extraction solvent is preferred.

Consequently, the results of this study revealed that the ultrasonication with THF was preferred to extract TCPP from polyurethane.

Concentrations of PFRs in chairs and car seat

The concentrations of PFRs in 5 samples of chairs and car seats extracted by the adequate extraction methods corresponding to the materials of the samples are shown in Figure 3. TCPP and TBP were detected from CS1-F

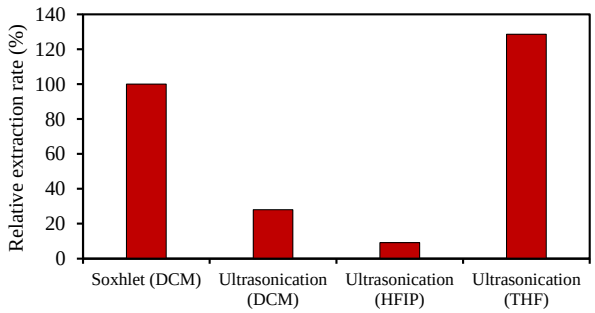

Figure 2: Effects of extraction methods on extraction rates.

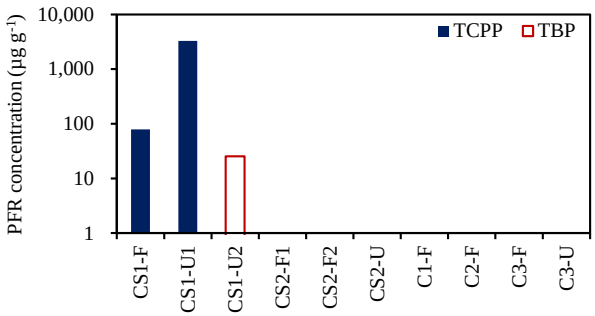

Figure 3: PFR concentrations in chairs and car seats.

(polyester) and -U1 (outside polyurethane which is attached with polyester fabric) and CS1-U2 (inside polyurethane), respectively. The concentrations of TCPP in CS1-F and -U1 were 78 and 3300 $\mu g \cdot g^{-1}$, respectively. The concentration of TBP in CS1-U2 was 25 $\mu g \cdot g^{-1}$. From the other samples, any PFRs targeted in this study were not detected. CS1 was constituted by polyester (CS1-F) and polyurethane (CS1-U1 and -U2), while CS2 was constituted by polyvinyl chloride (CS2-F) and polyurethane (CS2-U). Because polyvinyl chloride has the ability of fire retardant, the addition of PFRs to the material is not required. This could be a possible reason that PFRs were not detected from CS2.

In the previous study [11], PFRs in indoor airs of various indoor environments including cars, theaters, furniture stores, offices, and electronics stores in and around Zurich, Switzerland were measured and compared. The results revealed that the concentration of TCPP in a 9-year-old car showed the highest concentrations of PFRs in all the indoor environments. Given that TCPP in car seat could evaporate into indoor air, this result was in good agreement with that in this study.

This study confirmed that TCPP was present in a car seat. However, the sample number in this study was limited. A study to measure a larger number of car seats is required. Moreover, the dermal exposure rate of TCPP via direct contact of car seat with the skin should be calculated. Further studies are needed to assess comprehensive exposure amounts and risks of PFRs via inhalation, dust ingestion, and dermal exposure.

Acknowledgements
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