

Estimating Potential Dermal Exposure to Organophosphorus Flame Retardants via Direct Contact with Products

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Introduction

In indoor environments, organophosphorus compounds are contained in various products (e.g., car seat, chair, sofa, and curtain) as additives (e.g., flame retardant and plasticizer) at high concentration, some of which are toxic to human. Due to their low volatilities, it has been presumed that residents are orally exposed to them via indoor dust. However, our previous study revealed that the dermal exposure via indoor dust adsorbed onto the skin of residents could be comparable to the oral exposure. This also suggests that the dermal exposure via direct contact with products could result in a higher exposure rate than that via indoor dust due to an extremely high concentration of flame retardants in the products. In fact, we showed that the dermal exposure rate of triphenyl phosphate (TPhP) in nail polishes via direct contact estimated in accordance with the conventional estimation method for the dermal exposure was significantly higher than those of other exposure routes such as inhalation and dust ingestion. However, most conventional estimation methods are based on the dermal penetration experiment at low concentration, which is not supposed to estimate the dermal exposure rate via the direct contact with products whose chemical concentration is very high. In addition, the conventional method could not consider the effects of practical conditions (e.g., clothes and surface shape) on the dermal exposure rate.

As a device for the experimental determination of the dermal exposure rate, the EpiSkin epidermal model and human skin were investigated and applied for tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCPP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP)¹. According to their results, the absorption rates (ratio of absorbed quantity to application quantity in 24 h) of them were successfully determined by using the EpiSkin and were comparable to those using the human skin (TCEP: $3.7 \pm 2.5\%$, TCPP: $27.7 \pm 1.9\%$, TDCPP: $13.9 \pm 1.5\%$). However, these conventional devices require highly skilled professional techniques, and they are susceptible to error, hard to find, and very expensive.

On the other hand, a wristband made of silicon is used as a passive sampler to evaluate the exposure rates of semi volatile organic compounds (SVOCs) including polycyclic aromatic hydrocarbons and phosphorus compounds². The exposure rate determined by using the silicon wristband has a higher correlation with the urine concentrations of corresponding metabolites than that determined by a hand wipe method which is a typical analytical method to estimate the dermal exposure rate³. Given that silicon is cheaper and easier-to-use than the conventional devices to estimate the dermal exposure rate, it could be a suitable material for the device. However, in the previous study, the recovery rates of some organophosphorus compounds from the silicon wristband were low, and, as an example, that of TDCPP was 33%³. The improvement of analytical procedure, especially pretreatment procedure, is needed for a more accurate analysis.

In this study, to establish the device to estimate the dermal exposure rate via the direct contact with products, the optimization of the pretreatment procedure for the analysis of organophosphorus compounds in silicon was investigated. In addition, the practical migration experiment of organophosphorus compounds in a car seat to the silicon device via the direct contact with the device using the developed analytical method was carried out.

Materials and methods

Samples and chemicals

A silicon seat (5 cm × 5 cm, 0.5 cm thick) was used as a silicon device. Before use, it was ultrasonicated with ethyl acetate/methanol (1:1, v/v) for 15 min twice and then dried.

Fourteen organophosphorus compounds, trimethyl phosphate (TMP), triethyl phosphate (TEP), TCEP, triphenyl phosphine oxide (TPhPO), tripropyl phosphate (TPP), TCPP, TDCPP, TPhP, tributyl phosphate (TBP), cresyl diphenyl phosphate (CsDPhP), tris(2-butoxyethyl) phosphate (TBOEP), 2-ethylhexyl diphenyl phosphate (EHDPhP), tricresyl phosphate (TCsP), and tris(2-ethylhexyl) phosphate (TEHP) were determined. TBP-*d*₂₁ was used as an internal standard.

Recovery test

Mixed standards for the 14 organophosphorus compounds were added onto the silicon device. Then, it was extracted by the Soxhlet extraction method for 16 hours with 200 mL acetone/hexane (1:1, v/v). The extract was concentrated with an evaporator, and then the cleanup procedure was carried out. In this study, to optimize the cleanup procedure, the optimum conditions (i.e., type of column and amounts of washing and eluting solvents) were determined. The columns were conditioned with 10 mL dichloromethane/hexane (1:1, v/v) and 20 mL hexane. After the cleanup, the sample was concentrated by nitrogen purge, replaced with acetonitrile, and the internal standard was added. The analysis of organophosphorus compounds was carried out by a liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS).

Practical migration experiment

The silicon devices were placed on a car seat whose concentrations of organophosphorus compounds targeted in this study were preliminary determined. At predetermined times, the silicon devices were sampled and extracted in the same procedure as described above.

Results and discussion

Optimization of analytical procedure of organophosphorus compounds in silicon device

To determine the optimum cleanup method to analyze organophosphorus compounds in the silicon device, the effects of type of column and amounts of washing and eluting solvents on the recovery rates were investigated. Because Florisil column resulted in low recovery rate for TDCPP which is often used in a car seat³, a silica gel and sulfoxide columns were used in this study. After added the mixed standards onto the columns, the columns were washed with 10 mL hexane (Fraction 1), and then were eluted with 50 mL dichloromethane/hexane (1:1, v/v) and 10 mL dichloromethane (Fraction 2). The recovery rates using the silica gel column ranged 0% (TPhPO and TBOEP)–110% (EHDPHP). Those of 7 organophosphorus compounds targeted in this study (7 out of 14) were in the sufficient range (80%–120%). On the other hand, the recovery rates using the sulfoxide column ranged 42% (TMP)–168% (TBOEP). Those of 12 organophosphorus compounds targeted in this study (12 out of 14) were in the sufficient range. As a result, the sulfoxide column could be more suitable to analyze organophosphorus compounds than the silica gel column.

To determine the optimum amount of washing solvent, the silicone contents, which was determined as residue on evaporation, in washing solvents divided into 4 fractions (Fraction 1–4) were measured. The washing solvent was hexane, and each fraction was 10 mL. In Fraction 1 and 2, significant amounts of silicone were observed. However, no silicone was observed in Fraction 3 and 4. Therefore, 20 mL hexane was the optimum.

To determine the optimum amount of eluting solvent, the mixed standards added into the column were eluted with 10 mL dichloromethane/hexane (1:1, v/v) five times (Fraction 1–5) and 10 mL dichloromethane (Fraction 6). Thirteen organophosphorus compounds targeted in this study (13 out of 14) were eluted in Fraction 1 and 2 (the recovery rates ranged 80%–104%). The recovery rate of the other (TMP) in all the fractions was 48%. Consequently, 20 mL dichloromethane/hexane (1:1, v/v) was the optimum amount of the eluting solvent.

Using the optimum cleanup method determined, the recovery rates of organophosphorus compounds added onto the silicon device were determined. The results are shown in Figure 1. The recovery rates of most organophosphorus compounds (except for TPhPO) were out of the sufficient range. From the fractions of washing solvent including the high concentration of silicone, significant amounts of organophosphorus compounds were found. This result suggested that organophosphorus compounds were likely to be coeluted with washing solvent including silicone. Therefore, we tried to omit the cleanup procedure. The results are also shown in Figure 1. The recovery rates without cleanup were significantly higher than those with cleanup. Those of 7 organophosphorus compounds targeted in this study (9 out of 14) were in the sufficient range. This could be attributed the tendency of organophosphorus compounds to partition between silicone and acetonitrile (final solvent). Organophosphorus compounds were likely to exist in acetonitrile compared with silicon. It was concluded that no cleanup procedure was suitable to analyze organophosphorus compounds targeted in this study in the silicon device. It should be notice that cleanup procedure can be important in other cases (e.g., brominated flame retardants). The optimized work flow to estimate potential dermal exposure rates of the organophosphorus compounds using the silicone device is shown in Figure 2.

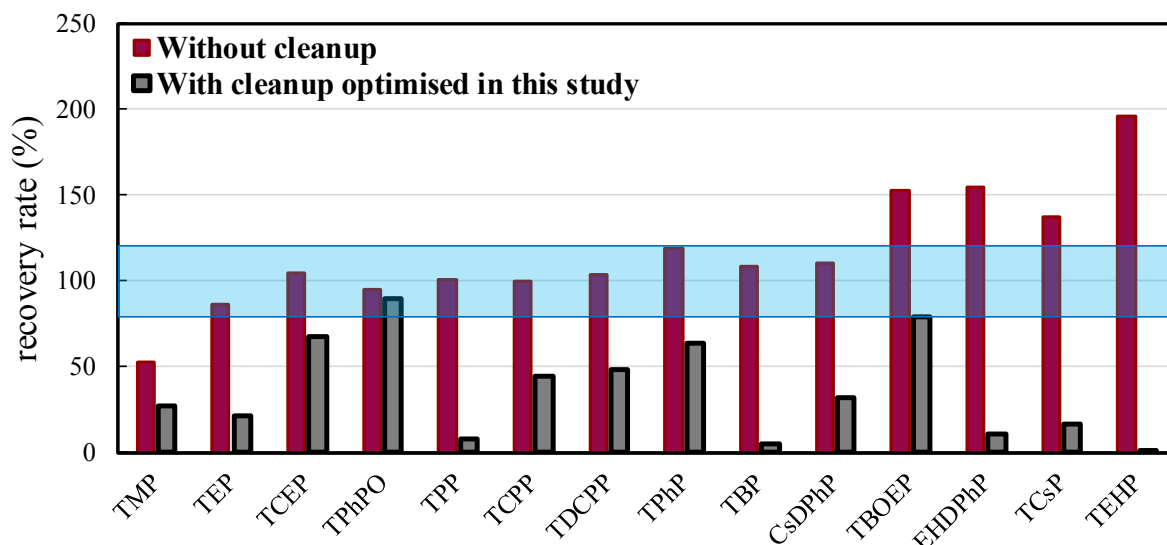


Figure 1: Recovery rates of organophosphorus compounds with and without cleanup

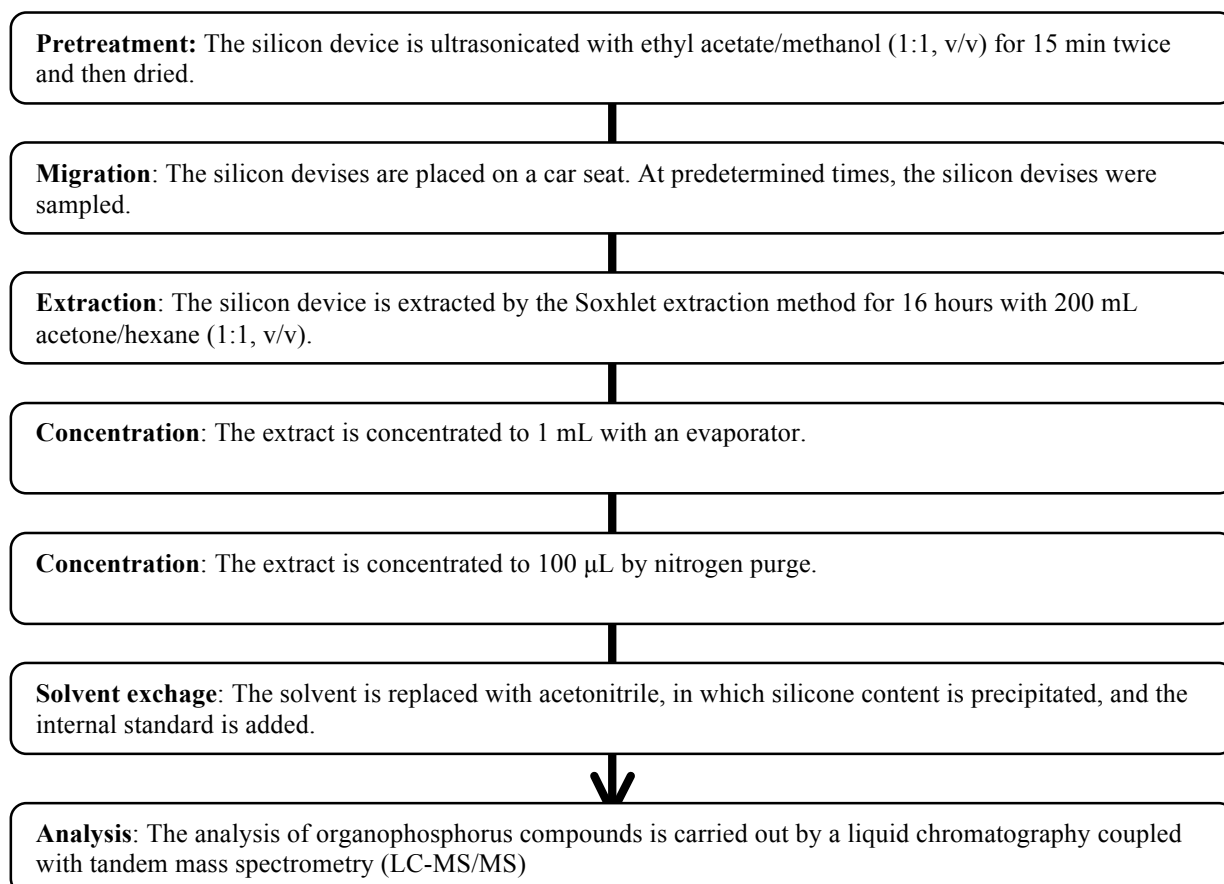


Figure 2: Optimized procedure to estimate potential dermal exposure rates of organophosphorus compounds via direct contact with products using silicone devise

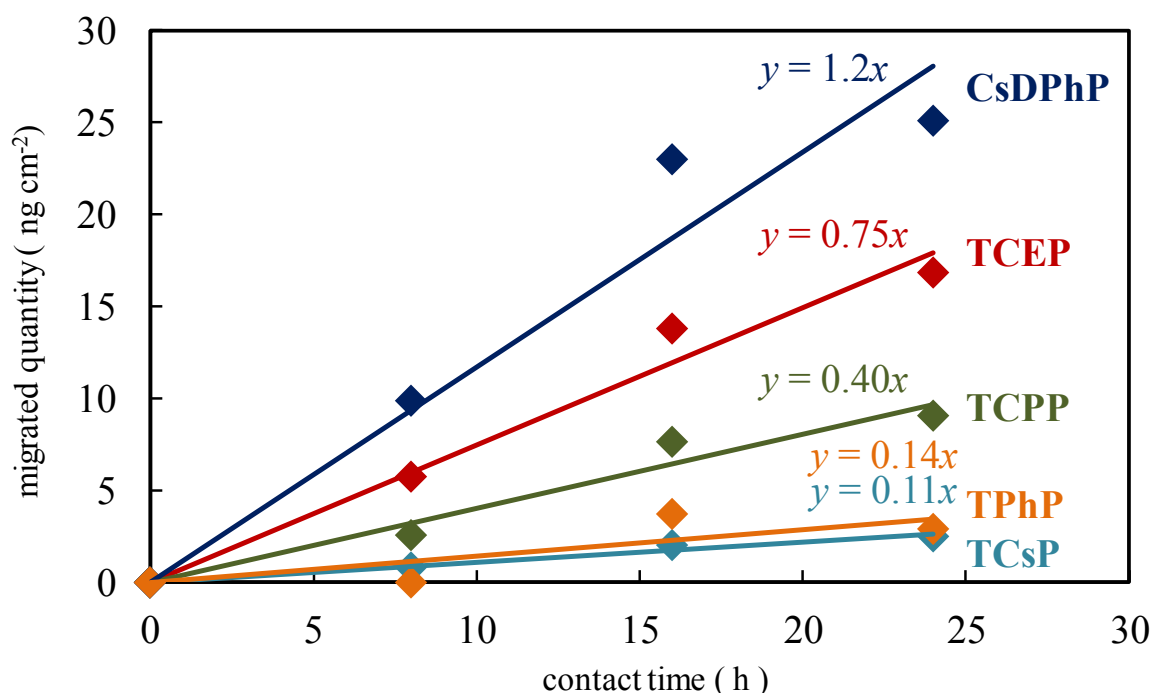


Figure 3: Migration rates of organophosphorus compounds from car sheet to silicone device

Practical migration experiment

The migration rates of organophosphorus compounds from the car sheet to the silicone device are shown in Figure 3. The concentrations of organophosphorus compounds in the car seat were 0.89 (CsDPhP), 0.15 (TPhP), 0.12 (TCEP), 0.07 (TCsP), and 0.03 (TCPP) wt%. The recovery rates of most organophosphorus compounds detected from the car seats (except for TCsP) were in the sufficient range. The migrated quantities of organophosphorus compounds in the silicone device linearly increased with contact time with the car seat. The migration rates of the organophosphorus compounds from the car seat to the silicone device were 1.2 (CsDPhP), 0.75 (TCEP), 0.40 (TCPP), 0.14 (TPhP), and 0.11 (TCsP) ng cm⁻² h⁻¹. The migration rates of the organophosphorus compounds which included in the car seats at higher concentration were likely to be higher. The driving force for the migration of the organophosphorus compounds from the car seat to the silicone is concentration difference. A higher concentration of the organophosphorus compound in the car seat resulted in a higher concentration of the organophosphorus compound at equilibrium, which in turn led to a larger concentration difference. As a result, an organophosphorus compound whose concentration in the car seats was high was likely to result in a higher migration rate.

In this study, to estimate the potential dermal exposure rate via the direct contact with products, we have established the analytical method for the organophosphorus compounds in the silicon device and carried out the migration experiment. The experimental results revealed that the proposed device and analytical method could be useful.

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