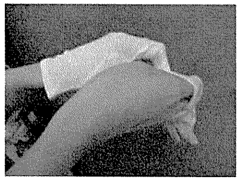
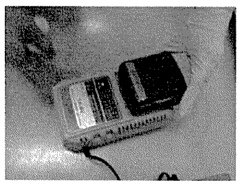
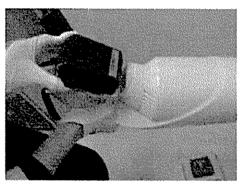
＜準備＞



1. 手袋をする



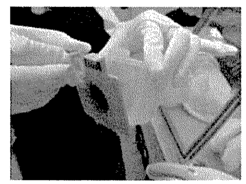
2. 電池パックを充電



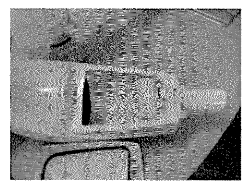
3. 電池パックを本体に装着

4. ダストバックを袋から取り出す

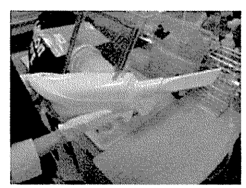
5. 逆止板を本体からはずす



6. ダストバッグを逆止板に取り付ける



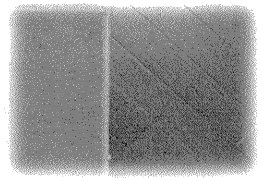
7. ダストバッグを本体に装着

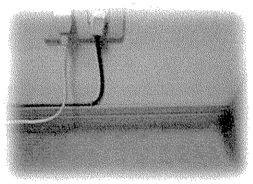


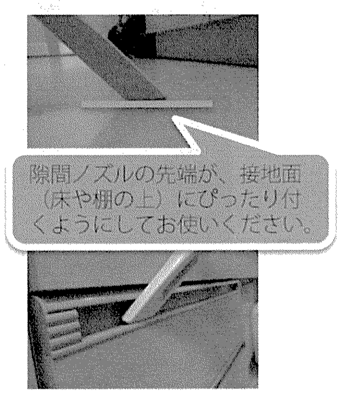
8. フタ及びスキマノズルを本体に装着

準備OK！

<サンプリング>



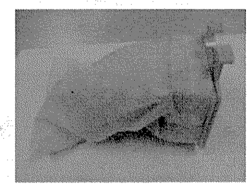




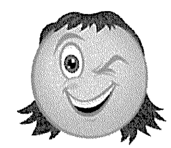
9. 部屋全体をまんべんなく

   カーペット
   フローリング
   部屋の隅
   テレビの裏
   本棚の上
   ・・・
   等から
   ホコリを沢山
   集めて下さい。

10. 途中でホコリのたまり具合を見て下さい。

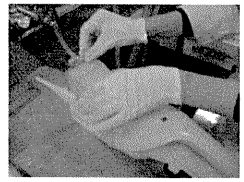


11. ダストバッグの2分の1以上になるようにホコリを集めて下さい。



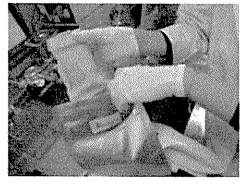
掃除機の強さは「強」
電池が切れたら充電して下さい。
一回の充電で連続して使用出来る時間は25分程度です。

＜サンプリングが終わったら＞

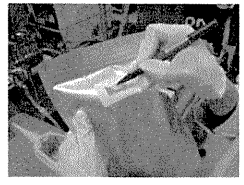


12. 逆止板とダストバッグを一緒に引き抜く

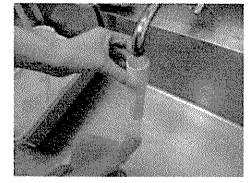
13. 逆止板を取り外す



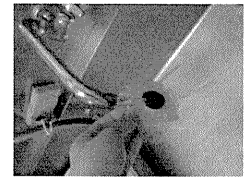
14. ダストバッグをラミジップ袋にしまう



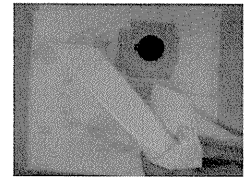
15. お名前、日付を記入



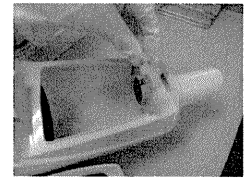
16. スキマノズルを洗う（水でかるく）



17. 逆止板を洗う（水でかるく）



18. 水分を拭く または乾燥させる



19. 逆止板を本体にセット

資料ーサンプリングマニュアル

ご協力ありがとうございました！

ご不安な点、ご質問などは03-3700-9298(神野又は香川)まで、
お気軽にご連絡下さい。

国立医薬品食品衛生研究所
生活衛生化学部第一室

神野透人　Hideto Jinno
香川聡子 Toshiko Kagawa

資料ーサンプリングアンケート

ハウスダスト中化学物質の実態調査
アンケート

＜国立医薬品食品衛生研究所　生活衛生化学部第一室＞

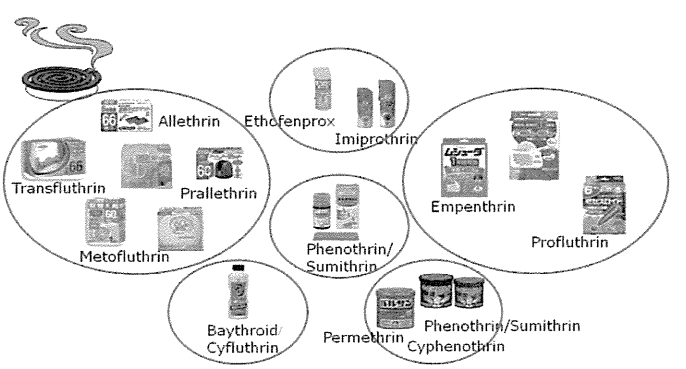
連絡先:東京都世田谷区上用賀 1-18-1
TEL&FAX:03-3700-9298
神野透人
香川聡子

今回の調査では、室内の化学物質汚染の実態を明らかにする目的で、ピレスロイド系薬剤、リン酸トリエステル等の可塑剤・難燃剤を測定対象としてハウスダストの分析を実施します。

ピレスロイド系薬剤に関しては、衣類用防虫剤や蚊取り製品を始め様々な家庭用殺虫剤やペット用のシャンプーに含まれている場合があります。また、可塑剤・難燃剤に関しては、家具や家電製品に含まれている可能性があります。従いまして、ご自宅でのこれら製品の使用状況についてお聞かせ下さい。

ご提供頂きました個人情報は適切に管理し、本調査目的以外には使用いたしません。また、第三者への提供・開示等は一切行いません。

何卒ご協力頂きますよう宜しくお願いいたします。



資料－サンプリングアンケート

日付＿＿＿＿ お名前＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿

ご住所 〒＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿

（番地はご記入頂かなくて結構です）

記入例:158-8501 東京都世田谷区上用賀１丁目

ホコリ採取時の状況について教えてください

★採取場所は？

・リビング及び寝室　・ワンルーム全体　・その他（　　）

★部屋の床の種類は？ いずれかに○　広さは？

・リビング

フローリング　・フローリング+一部カーペット　・畳のみ　・畳+一部カーペット　・全面カーペット

その他（　　）　広さ　およそ＿＿＿＿畳　または＿＿＿＿m²

・寝室

フローリング　・フローリング+一部カーペット　・畳のみ　・畳+一部カーペット　・全面カーペット

その他（　　）　広さ　およそ＿＿＿＿畳　または＿＿＿＿m²

・ワンルームの部屋

フローリング　・フローリング+一部カーペット　・畳のみ　・畳+一部カーペット　・全面カーペット

その他（　　）　広さ　およそ＿＿＿＿畳　または＿＿＿＿m²

★ホコリを吸引したおおよその時間は？

床　およそ＿＿＿＿分

棚上　およそ＿＿＿＿分

資料ーサンプリングアンケート

★一番最近掃除をしたのはいつですか？ いずれかに○

昨日　・1週間前　・1か月前　・半年前　・それ以前

★その時の掃除方法は？ 当てはまるものいくつでも○

掃除機　・ほうき　・クイックルワイパー　・雑巾　・その他(　　)

★ワックスがけをしていますか？ いずれかに○

はい（一番最近いつ？→_____）　・いいえ

★換気時間等について当てはまるものいくつでも○

・1日中窓あけっぱなし　・1日合計(_____時間)窓開けている

・機械換気(1日_____時間)　・空気清浄機(1日_____時間)

★ご自宅での喫煙の有無

・無し　・有り（・室内　・室外　）

★ペットを飼っていますか？ 飼っている場合はその種類を教えてください。

・飼っていない　・飼っている(室内 室外)(種類:　　)

★ペットを飼っている方にお伺いいたします。トリミングやにおいのケアはどうされていますか？

例）月に一回シャンプー(ライオン のみ取りリンスインシャンプー)している。においは精油をスプレーしている。

〔　　〕

★サンプリングの際に何か問題や気付いた点がありましたらご記入ください

例）床なのか隙間なのか判断に迷った場所、充電や時間的な問題で2周できなかった、

〔　　〕

資料ーサンプリングアンケート

シロアリ駆除及びガーデニング用薬剤の使用について

★お住まいの住宅及び庭でご使用の防虫剤・殺虫剤について教えて下さい。

		使用又は処理状況
	シロアリ駆除	□（　　）
		例 ☑（4ヶ月前に処理　有効成分　ジノフラテン他）
	園芸用殺虫剤	□（　　）
		例 ☑（ベニカスプレー　週一回散布　　）
	その他	□（　　）
		□（　　）
		□（　　）
		□（　　）

資料ーサンプリングアンケート

殺虫剤等の使用について

★サンプリングして頂いたお部屋でご使用の防虫剤・殺虫剤について教えて下さい。

		使用状況
	衣類用防虫剤	□( )
	記入例	☑(ムシューダ、タンス引出に合計 20 個くらい)
	蚊取り (液体蚊取り)	□( )
	記入例	☑(アースノーマット、居間で 7 月から 9 月ほとんど毎日 8 時間程度使用)
	蚊取り (ファン式蚊取り)	□( )
	記入例	☑(蚊に効くカトリス寝室で 7 月から 9 月ほとんど毎日 8 時間程度使用)
	燻煙剤	□( )
	記入例	☑(バルサン、2 週間に 1 回位)
	エアゾール (ゴキブリ用)	□( )
	記入例	☑(ゴキジェットプロ、1 ヶ月に 3 回くらい)
	エアゾール (ダニ・ノミ用)	□( )
	記入例	☑(ダニアース、1 ヶ月に一回)
	その他	□( )
		□( )
		□( )
		□( )

資料ーサンプリングアンケート

家具及び家電製品について

★サンプリングして頂いたお部屋にある家具・家電製品(使用期間)について教えて下さい。
この他にもなにかプラスチックの製品や大きなものがありましたらご記入下さい。

		リビング	寝室	ワンルーム
	カーテン	防炎加工 (有り　無し)	防炎加工 (有り　無し)	防炎加工 (有り　無し)
	カーペット	防炎加工 (有り　無し)	防炎加工 (有り　無し)	防炎加工 (有り　無し)
例	テレビ	☑(液晶、32インチ、3年目)	☑(ブラウン管、20インチ)	□( )
例	冷蔵庫	□( )	□( )	☑(500 L、2年目)
	テレビ	□( )	□( )	□( )
	冷蔵庫	□( )	□( )	□( )
	エアコン	□( )	□( )	□( )
	パソコン	□( )	□( )	□( )
	プリンター	□( )	□( )	□( )
	机	□( )	□( )	□( )
	本棚	□( )	□( )	□( )
	食器棚	□( )	□( )	□( )
	空気清浄機	□( )	□( )	□( )
	ベッド	□( )	□( )	□( )
	タンス	□( )	□( )	□( )
	ソファ	□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )

資料ーサンプリングアンケート

噴霧式型の家庭用品等の使用について

★サンプリングして頂いた部屋でご使用の家庭用品について教えて下さい。
この他にもなにか使用している家庭用品がありましたらなんでも記入して下さい。

		リビング	寝室	ワンルーム
例	消臭芳香剤(スプレー)	☑(リセッシュ、1日1回)	☑(ファブリーズ、週1回)	□( )
	消臭芳香剤(スプレー)	□( )	□( )	□( )
	消臭芳香剤(置き型)	□( )	□( )	□( )
	スプレー式整髪料	□( )	□( )	□( )
	スプレー式制汗剤	□( )	□( )	□( )
	化粧品	□( )	□( )	□( )
	香水	□( )	□( )	□( )
	その他	□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )
		□( )	□( )	□( )

☺ ご協力ありがとうございました！

III. 研究成果の刊行に関する一覧表

研究成果の刊行に関する一覧表

発表者氏名	論文タイトル名	発表誌名	巻号	ページ	出版年
Kawakami, T., Isama, K., Matsuoka, A.	Analysis of phthalic acid diesters, monoester, and other plasticizers in polyvinyl chloride household products in Japan.	T. Environ. Sci. Health Part A,	46	855-864	2011
Kawakami T., Isama K., Jinno H., Matsuoka A. and Nishimura T.	Transfer of phthalic acid diesters from model PVC sheet to skin surface.	Organo-Halogen Compounds	73	1116-1119	2011
酒井康行, 小森喜久夫	ヒトハザード評価における新しい流れと課題.	自動車研究	33	9-14	2011

IV. 研究成果の刊行物・別刷

Journal of Environmental Science and Health Part A (2011) **46**, 855–864
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ISSN: 1093-4529 (Print); 1532-4117 (Online)
DOI: 10.1080/10934529.2011.579870

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Analysis of phthalic acid diesters, monoester, and other plasticizers in polyvinyl chloride household products in Japan

TSUYOSHI KAWAKAMI[1], KAZUO ISAMA[1] and ATSUKO MATSUOKA[2]

[1]*Division of Environmental Chemistry, National Institute of Health Sciences, Tokyo, Japan*
[2]*Division of Medical Devices, National Institute of Health Sciences, Tokyo, Japan*

The aim of this study was to determine the concentrations of six phthalic acid diesters (PAEs) [di(2-ethylhexyl) phthalate (DEHP), di-*n*-butyl phthalate (DBP), butyl benzyl phthalate (BBP), diisononyl phthalate (DINP), di-*n*-octyl phthalate (DNOP), and diisodecyl phthalate (DIDP)], two non-phthalic plasticizers [di(2-ethylhexyl) adipate (DEHA), 2,2,4-trimethyl-1,3-pentanediol diisobutylate (TMPDIB)], and mono 2-ethylhexyl phthalate(MEHP) in polyvinyl chloride (PVC) household products that children often places in their mouths and/or contact with their skin (41 products, 47 samples) in Japan. The detection frequencies of the studied compounds were as follows: DEHP (79 %), DINP-2 (13 %), DINP-1 (11 %), DBP (8.5 %), DEHA (8.5 %), DIDP (4.3 %), and DNOP (2.1 %). Concentrations of these compounds ranged from 0.021 % to 48 %. BBP and TMPDIB were not detected in the all samples. Most samples contained DEHP and DINP at high concentrations over 0.1 %. High concentrations of PAEs were detected in PVC household products that appear appealing to children and can possibly be licked and chewed by them. Di(2-ethylhexyl) terephtalete, diisononyl 1,2-cyclohexanedicarboxylic acid, acetyl tributyl citrate, and di(2-ethylhexyl) 4-cyclohexene-1,2-dicarboxylate used as substitute plasticizers were also detected in several samples. MEHP was present in 70 % of the samples, with concentrations ranging from trace amounts to 140 μg/g. The ratios of MEHP against DEHP were 6.2×10^{-4} to 1.6×10^{-1} %. MEHP in the household products investigated in this study was most probably an impurity in DEHP. The high concentrations of PAEs detected in products that children often place in their mouth reveal the importance of replacing plasticizers in common household products, and not just children's toys, with safer alternatives.

Keywords: Phthalic acid diester and monoester, plasticizer, polyvinyl chloride, household products.

Introduction

Phthalic acid diesters (PAEs) are widely used as plasticizers in various products, particularly those made from polyvinyl chloride (PVC). In 2009, Japan produced 197,930 tons of PAEs annually,[1] including 125,281 tons of di(2-ethylhexyl) phthalate (DEHP), 59,822 tons of diisononyl phthalate (DINP), 4,041 tons of diisodecyl phthalate (DIDP), and 1,216 tons of di-*n*-butyl phthalate (DBP).

Since PAEs easily migrate from plastic products and their content in plastic material is high, many toxicological investigations of PAEs have been carried out in order to determine whether they have an adverse effect on human health. Reproductive and developmental toxicities of DEHP, DBP, and butyl benzyl phthalate (BBP) have been reported in rats and mice.[2–4] Although testicular toxicity of DINP has not been observed, its hepatic toxicity has been reported in rats.[5] When male and female marmosets were treated with DEHP by oral gavage from weaning to sexual maturity, no histological changes were observed in them,[6] indicating that toxicological sensitivity is different between primates and rodents for some unknown reason.

In vitro percutaneous absorption rates of DEHP and DBP are slower for humans than rats;[7,8] further, patch tests of DEHP, DINP, and DIDP revealed no skin sensitization potential.[9] However, contact dermatitis from the DBP and benzalkoniunm chloride in Timodine® has been reported.[10] Furthermore, both DBP and DEHP displayed adjuvant effects during contact and atopic dermatitis.[11]

In 1999, the European Union (EU) temporarily restricted the use of DEHP, DBP, BBP, DINP, DIDP, and di-*n*-octyl phthalate (DNOP) in toys and childcare goods intended to be placed in the mouth of children under 3 years old.[12] In 2005, this decision was amended to limit DEHP, DBP, and BBP to less than 0.1 % in all plastic toys and childcare products and DNOP, DINP, and DIDP to less than 0.1 % in products that children can place in their mouth.[13] In 2003, DEHP was restricted by the Food Sanitation Law of Japan to below 0.1 % in the plastic containers

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that come into with food and in toys for preschool children (under 6 years old) and DINP was restricted in products that children can place in their mouth.[14]

Amending this regulation to be similar to the current EU regulation is currently under consideration in Japan.[15–17] Although it is considered that the exposure of children to PAEs in toys and childcare products has been reduced, oral PAE exposure can occur from licking and chewing plastic household products that are not included in the list of regulated products. Exposure may also occur from hand-to-mouth contact with households products, similar to what has been found for brominated flame retardants (BFRs) and perfluoroalkyl compounds present in household products .[18,19] However, relatively little is known about the concentrations of PAEs in household products[20,21] compared to that in toys for preschool children.[22–24]

In this study, therefore, we attempted to elucidate the concentrations of the six PAEs regulated in the EU in household products made with PVC that children can place in their mouth and can come in contact with their skin. Furthermore, we determined the concentrations of di(2-ethylhexyl) adipate (DEHA) and 2,2,4-trimethyl-1,3-pentanediol diisobutylate (TMPDIB), both of which are compounds used as replacements for PAEs.[21] Phthalic acid monoesters are major toxic metabolites of PAEs.[3,4] Recently, the presence of mono 2-ethylhexyl phthalate (MEHP), one such phthalic acid monoester, in house dust was reported.[25] However, since only a few studies have investigated MEHP in PVC products,[26] we determined the concentrations of MEHP in household products in this study.

Materials and methods

Samples

Household products made from PVC were purchased from several retail and online stores in Japan from September 2009 to February 2010. A total of 41 products (47 samples) were analyzed. They were divided into classes on the basis of usage and separated by color and flexibility as much as possible (Table 1).

Materials

Environmental grade DBP, DEHP, BBP, and DEHA were obtained from Kanto Chemical Co., Inc.(Tokyo, Japan). DNOP, DIDP, and TMPDIB were obtained from Fluka (Buchs, Switzerland), Dr. Ehrenstorfer GmbH (Augsburg, Germany), and Tokyo Chemical Ind., Co., Ltd. (Tokyo, Japan), respectively. Deuterated PAEs (DBP, DEHP, BBP, and DNOP), and anthracene-d_{10} were obtained from Kanto Chemical Co., Inc.. MEHP and MEHP-d_4 were obtained from Hayashi Pure Chemical Ind., Ltd. (Osaka, Japan), and the isomers DINP-1 (CAS.68515-48-0) and DINP-2 (CAS. 28553-12-0) were obtained from Kanto Chemical Co., Inc., and Wako Pure Chemical Ind., Ltd. (Osaka, Japan), respectively. DINP-1 and 2 contained different kinds of isomers.[5] Pesticide residue grade acetone, hexane, ethyl acetate, and diethyl ether were obtained from Wako Pure Chemical Ind., Ltd., Kanto Chemical Co., Inc., and Sigma-Aldrich (St. Louis, MO, USA). HPLC grade acetonitrile was obtained from Kanto Chemical Co., Inc. Phthalate analysis grade sodium chloride and anhydrous sodium sulfate, analytical grade sodium hydroxide, and heavy metal analysis grade hydrochloric acid were obtained from Wako Pure Chemical Ind., Ltd. Deionized water was produced by Milli-Q Synthesis A10 (Millipore, Tokyo, Japan). All utensils made of glass, metal, or Teflon were heated at 250°C for more than 12 h to prevent contamination.

Sample processing

PAEs, DEHA, and TMPDIB were processed and analyzed as previously described[27] with minor modifications. The sample was cut and 0.1 g of the sample was placed into a glass tube, with 3 mL of acetone/hexane = 3/7 (v/v) and left overnight at 37°C. The volume of the sample solution was adjusted to 10 mL and diluted to the appropriate volume (100–5000-fold). Finally, 50 μL of an acetone solution containing 2 μg mL^{-1} of the internal standard (DNOP-d_4, 0.2 μg mL^{-1}) was added to 1 mL of the diluted sample solution, and this solution was analyzed by gas chromatography/mass spectrometry (GC/MS). The concentrations of DINP and DIDP were determined using the sum of total peak area of their isomers similar to previous studies.[22,24,28]

A blank test was performed concurrently to rule out the possibility of contamination with PAEs during sample processing. PAEs [DBP (0.05 %), BBP (0.05 %), DEHP (0.05 %), DNOP (0.05 %), DINP (0.2 %), and DIDP (0.2 %)], DEHA (0.05 %), and TMPDIB (0.05 %) were added to the sample that did not contain the compounds studied, and GC/MS analysis was performed with the 100-fold diluted sample to obtain the recovery, method detection limit (MDL), and method quantification limit (MQL). MDL[29] and MQL[30] were calculated as follows:

$$\mathrm{MDL} = 3.3 \times \rho/\mathrm{ar} \quad (1)$$

$$\mathrm{MQL} = 10\rho \quad (2)$$

where ρ is the standard deviation obtained from the results of a low-concentration analysis; a is the slope of the standard curve; and r is the relative sensitivity. The obtained recoveries, MDL, and MQL are listed in Table 2.

MEHP was analyzed as described[26] with minor modifications. A 50 μL of acetone solution containing 2 μg mL^{-1} of the surrogate standard MEHP-d_4 was added to 1 mL of the extracted sample solution. The solution was dried using a gentle N_2 stream, and the residue was dissolved in 1 mL

Table 1. List of the PVC household products studied.

Usage	*Name of products*		*Country*	*Sample Name*
Stationery	card case		China	A1
	card case		China	A2
	eraser		Vietnam	A3
	card case		China	A4
	card case		China	A5
	cutting mat		Taiwan	A6
	eraser		Japan	A7
	eraser		Japan	A8
	eraser		Japan	A9
	desk mat		Japan	A10
	clip		China	A11
Accessories and others	shower cap[a]		Vietnam	B1
	emblem of rain coat		China	B2
	non-slip hook of baby carriage		China	B3
Outdoor and sports goods	ball		China	C1
	ring float	mouthpiece	China	C2_1
		body (clear)		C2_2
		body (blue)		C2_3
	beach ball	mouthpiece	China	C3_1
		body		C3_2
	shuttlecock	head	China	C4_1
		case		C4_2
	ball		unknown	C5
	ball		Taiwan	C6
	yoga mat		China	C7
Small articles	case		China	D1
	card holder		China	D2
	pass case	synthetic leather	China	D3_1
		clear part		D3_2
	key cover		China	D4
	mobile phone strap[b]	tag	Korea	D5_1
		body		D5_2
	mobile phone strap[b]		unknown	D6
	mobile phone strap[b]		Japan	D7
	mobile phone strap[b]		China	D8
	key holder		Japan	D9
Furniture aids	edge cover		China	E1
	sucking disc		China	E2
	floor mat		Japan	E3
	floor mat		Japan	E4
	edge cover (ball type)		China	E5
	casement lock		China	E6
	edge cover		China	E7
Furniture	children sofa		China	F1
	pipe chair		China	F2
	cushion		China	F3
	children chair		Vietnam	F4

[a]According to FT-IR analysis, PVC might not be used or might not be the dominant material for shower cap (B1), although the label on the products reads "PVC and others."
[b]Liquid crystal display (LCD) cleaner type.

of acetonitrile. Then, 5 % sodium chloride solution (3 mL) and 0.01 mol L^{-1} sodium hydroxide solution (0.5 mL) were added in the sample solution. Next, 2 mL of hexane was added to the sample solution and the mixture was shaken by hand for 5 min to remove excess PAEs. After shaking, the sample solution was centrifuged for 2 min (3000 rpm) and the hexane phase was disposed. This extraction procedure was repeated 4 times. Then, the pH of the sample solution was adjusted to pH 3 with 0.01 mol L^{-1} hydrochloric acid. Next, 2 mL of ethyl acetate was added in the sample

Table 2. GC retention times, quantifying and quabfying ions, recoveries (%) and its coefficients of variation (C,V,%) (n=3) and MDL[a] and MQL[b] of the compounds studied.

	M.W.	*Retention time (min)*	*Quantifying ion (m/z)*	*Qualifying ion (m/z)*	*Recovery*	*C.V.*	*MDL*	*MQL*
Phthalate diesters[c]								
DBP	278.3	11.68	149	223	100	0.74	0.00021	0.0038
BBP	312.4	13.53	149	206	101	1.9	0.00049	0.0099
DEHP	390.6	14.24	149	167	109	1.8	0.00061	0.0098
DNOP	390.6	15.04	279	149	86	2.0	0.0047	0.0086
DINP-1	418.6	14.8–15.8	293	149	102	1.3	0.0064	0.026
DINP-2	418.6	15–16	293	149	100	2.9	0.0075	0.059
DIDP	446.7	15.2–16.8	307	149	106	2.4	0.011	0.052
Others[d]								
TMPDIB	286.4	9.63	71	243	98	2.3	0.0017	0.011
DEHA	370.6	13.63	129	147	88	2.0	0.0062	0.0087
Internal standard								
DBP-d_4	282.3	11.66	153					
BBP-d_4	316.4	13.52	153					
DEHP-d_4	394.6	14.21	153					
DNOP-d_4	394.6	15.01	153					
Anthracene-d_{10}	188.3	11.02	188					
Mono ethylhexyl phthalate[e]								
MEHP	278.3	12.02	163	149,181	76	4.0	0.029	1.5
MEHP-d_4	282.3	12.01	167					

[a]MDL: (3.3 × standard deviation)/(slope of calibration curve × relative sensitivity), Unit: PAEs, DEHA and TMPDIB (%), MEHP ($\mu g\ g^{-1}$).
[b]MQL: 10 × standard deviation, Unit: PAEs, DEHA and TMPDIB (%), MEHP ($\mu g\ g^{-1}$).
[c]DBP, BBP, DEHP and DNOP were quantified using corresponding deuterated compounds as internal standard, DINP and DIDP were quantified using DNOP-d_{10} as internal standard.
[d]TMPDIB and DEHA were quantified using anthracene-d_{10} as internal standard.
[e]MEHP was quantified using MEHP-d_4.

solution. The mixture was shaken by hand for 5 min and the ethyl acetate layer was separated from the aquatic phase by centrifugation for 2 min (3000 rpm).

This extraction procedure was performed twice and the ethyl acetate layer was combined and dehydrated with anhydrous sodium sulfate. The dehydrated solution was evaporated and dried under gentle N_2 stream. The residue was dissolved in 1 mL of acetone, and MEHP was methylated with diazomethane-diethyl ether.[31] After the methylation procedure, the sample solution was dried under gentle N_2 stream and the residue was dissolved in 1 mL of acetone. Finally, 50 μL of acetone solution containing 2 $\mu g\ mL^{-1}$ of anthracene-d_{10} used for confirmation of recovery of the surrogate standard was added, and this solution was then analyzed by GC/MS. MEHP was quantified by MEHP-d_4, and a blank test was performed in the same manner as that described above. MEHP was added to the sample (5 $\mu g\ g^{-1}$), and the recovery, MDL, and MQL were obtained in the same manner to that described above. These values are shown in Table 2.

GC/MS analysis

All samples in this study were analyzed using a Focus GC with a DSQII MS (Thermo Fisher Scientific, Waltham, MA, USA). A DB-5MS fused silica capillary column (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 μm, Agilent, Santa Clara, CA, USA) was used for analysis in this study. The carrier gas used was He with a flow rate of 1.0 mL min^{-1}. The temperatures of the injector, transfer line, and ion source were 230, 280, and 250°C, respectively. The sample was injected in the splitless mode and the injected volume was 1 μL. The GC oven temperature was initially maintained at 60°C for 2 min and the temperature increased to 310°C at a rate of 20°C min^{-1}. The oven temperature was then maintained at 310°C for 10 min. The MS was operated in the electron ionization (EI) mode at 70 eV and the analysis was performed using the selected ion monitoring (SIM) mode. The retention times and the quantifying and qualifying ions are listed in Table 2.

Results and discussion

Concentrations of PAEs, DEHA and TMPDIB in the PVC household products

The concentrations of PAEs, DEHA and TMPDIB in the PVC household products are listed in Table 3. The concentration range, detection number, and detection frequency of PAEs, DEHA, and TMPDIB are listed in Table 4. The following PAEs were detected at high frequency: DEHP was present in 79 % of samples (concentration range: 0.021–47 %), DINP-2 in 13 % (0.075–48 %), DINP-1 in 11 %

Table 3. Concentrations of PAEs(%), TMPDIB(%), DEHA(%), and MEHP($\mu g\ g^{-1}$) in the PVC household products.

Usage	*Sample Name*	*DBP*	*BBP*	*DEHP*	*DNOP*	*DINP-1*	*DINP-2*	*DIDP*	*TMPDIB*	*DEHA*	*MEHP*
Stationery	A1	–[a]	–	0.021	–	–	–	–	–	–	–
	A2	–	–	17	–	–	–	–	–	–	6.4
	A3	–	–	41	–	–	–	–	–	–	20
	A4	–	–	–	–	–	–	–	–	–	–
	A5	–	–	19	–	–	–	–	–	–	6.6
	A6	–	–	17	0.26	–	1.8	1.4	–	0.32	75
	A7	18	–	30	–	–	–	–	–	–	8.9
	A8	7.4	–	35	–	–	–	–	–	–	51
	A9	17	–	29	–	–	–	–	–	–	7.3
	A10	–	–	21	–	–	–	–	–	–	tr[b]
	A11	–	–	11	–	–	–	–	–	–	5.2
Accessories and others	B1	–	–	–	–	–	–	–	–	–	–
	B2	–	–	0.88	–	–	27	–	–	–	–
	B3	–	–	19	–	–	–	–	–	–	11
Outdoor and Sports goods	C1	–	–	–	–	0.58	–	–	–	–	–
	C2_1	–	–	0.097	–	–	0.075	–	–	–	–
	C2_2	–	–	–	–	–	–	–	–	–	–
	C2_3	–	–	–	–	–	–	–	–	–	–
	C3_1	–	–	–	–	–	–	–	–	–	–
	C3_2	–	–	–	–	–	–	–	–	0.052	–
	C4_1	–	–	32	–	–	–	–	–	–	37
	C4_2	–	–	0.076	–	–	–	–	–	–	–
	C5	–	–	–	–	–	–	–	–	0.035	–
	C6	–	–	37	–	–	–	–	–	–	21
	C7	0.52	–	18	–	–	–	–	–	–	23
Small articles	D1	–	–	13	–	–	–	–	–	–	7.0
	D2	–	–	24	–	–	–	–	–	–	13
	D3_1	–	–	16	–	8.7	–	–	–	–	3.7
	D3_2	–	–	15	–	–	–	–	–	–	3.5
	D4	–	–	–	–	–	–	–	–	–	–
	D5_1	–	–	10	–	35	–	–	–	–	12
	D5_2	–	–	18	–	–	–	–	–	–	9.3
	D6	–	–	26	–	–	–	–	–	–	1.6
	D7	–	–	7.0	–	–	1.8	5.8	–	0.41	110
	D8	–	–	8.7	–	8.5	–	–	–	–	6.1
	D9	–	–	–	–	–	–	–	–	–	–
Furniture's aids	E1	–	–	23	–	–	–	–	–	–	13
	E2	–	–	1.5	–	–	48	–	–	–	tr
	E3	–	–	36	–	–	–	–	–	–	63
	E4	–	–	27	–	–	–	–	–	–	63
	E5	–	–	30	–	–	–	–	–	–	30
	E6	–	–	12	–	12	–	–	–	–	14
	E7			47							30
Furniture	F1	–	–	21	–	–	–	–	–	–	140
	F2	–	–	16	–	–	1.5	–	–	–	2.1
	F3	–	–	25	–	–	–	–	–	–	24
	F4	–	–	20	–	–	–	–	–	–	20

[a]Not detected.
[b]Between MDL and MQL.

(0.58–35 %), DBP in 8.5 % (0.52–18 %), DIDP in 4.3 % (1.4–5.8 %), DNOP in 2.1 % (0.26 %). The total detection frequency of DINP (DINP-1 + DINP-2) was 23 %. DEHA was detected in 4 samples (0.035–0.41 %). Recently, Abe et al. reported that the detection frequency of PAEs in PVC toy products was 32 %,[32] which is lower than that reported in a previous study[24] conducted in Japan in 2001. Furthermore, they also found a high detection frequency of TMPDIB (48 %) in PVC toy products in Japan.[32] However, the detection frequency of PAEs in household products considered in this study was still higher than that in PVC toy products.