Analysis of Monomeric and Oligomeric Phosphate Esters in Indoor Air and House Dust by GC-MS and LC-MS

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Introduction

Organophosphorus chemicals (OPCs) are widely applied in industrial products such as plasticizers, insulator, and flame retardants. The Japanese consumption of OPCs for flame retardants in 2004 has been estimated at 30 500 t, because of the worldwide restriction of the use of halogenated products. The direct exposure of OPCs to human by means of the vaporization to indoor air and the adsorption on house dust from these products is a matter of concern as same as other flame retardants. Nevertheless, the information about the contamination levels and behavior of OPCs in indoor air and house dust is still limited.

In this study, analytical methodology for 13 monomeric phosphate esters such as trimethyl phosphate (TMP), triethyl phosphate (TEP), tripropyl phosphate (TPrP), tributyl phosphate (TBP), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloroisopropyl) phosphate (TCIPP), tris(2-ethylhexyl) phosphate (TEHP), tris(1,3-dichloro-2-propyl) phosphate (TDCPP), tris(butoxyethyl) phosphate (TBEP), triphenyl phosphate (TPhP), cresyldiphenyl phosphate (CDP), tricresyl phosphate (TCP), and trixylenyl phosphate (TXP)), and 4 oligomeric phosphate esters (resorcinol bis(diphenyl phosphate) (RDP), resorcinol bis(dixylenyl phosphate) (RDX), bisphenol A bis(diphenyl phosphate) (BDP), and polyoxyalkylene bis(dichloroalkyl phosphate) (CR-504L) in indoor air and house dust by using GC-MS and LC-MS was developed.

Materials and Methods

TMP, TEP, TBP, TCEP, TCIPP, TEHP, TBEP, TDCPP, TPhP, and TCP were purchased from Wako Pure Chemical Industries, Japan, TPrP was purchased from Sigma-Aldrich, MO, USA, CDP was purchased from Tokyo Chemical Industry, Japan, and TXP, RDP, RDX, BDP, and CR-504L were obtained from Daihachi Chemical Industry, Japan. Deuterium labeled OPCs used as the surrogate substances such as triethyl phosphate (D_{15}, 99%) (TEP-d_{15}), tributyl phosphate (D_{27}, 99%) (TBP-d_{27}), tris(2-chloroethyl) phosphate (D_{12}, 99%) (TCEP-d_{12}), tris(2-ethylhexyl) phosphate (D_{51}, 99%) (TEHP-d_{51}), triphenyl phosphate (D_{15}, 99%) (TPhP-d_{15}), tricresyl phosphate (D_{21}, 99%) (TCP-d_{21}), and tris(3,5-dimethylphenyl) phosphate (D_9, 99%) (3,5-TXP-d_9) were purchased from Hayashi Pure Chemical Industries, Japan.

Indoor air was collected using a quartz fiber filter (QFF, 47 mmΦ, Whatman, UK) and a Empore Disk C18 FF (47 mmΦ, 3M, MN, USA) at a flow of 10 L/min for 2 h. Fig. 1 shows the Teflon holder for QFF and Empore Disk C18 FF, which was purchased from GL Sciences, Japan. QFF and Empore Disk C18 FF were ultrasonic-extracted with acetone for 10 min. House dust was collected with clearing of

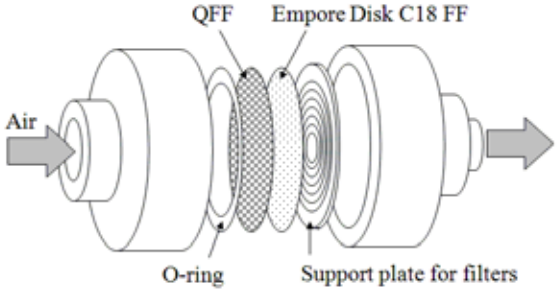

Fig. 1. Teflon holder for QFF and Empore Disk C18 FF.

wood, stone, hair, paper, and metal etc. 0.2 g of house dust were Soxhlet extracted with acetone for 6 h and with toluene for 16 h.

13 monomeric phosphate esters were measured by GC-MS after the addition of surrogate substances to these extracts and the purification of these extracts with a column containing 0.5 g of Wakogel S-1 (Wako Pure Chemical Industries, Ltd., Japan). The GC-MS measurements were performed with Shimadzu GCMS-QP2010 Plus equipment with a DB-WAX column (30 m x 0.25 mm i.d., film thickness 0.25 µm, Agilent, USA) for TMP, TEP, and TPrP, and with a DB-17MS column (30 m x 0.25 mm i.d., film thickness 0.25 µm, Agilent, USA) for TBP, TCEP, TCIPP, TEHP, TBEP, TDCPP, TPhP, CDP, TCP, and TXP. The temperature conditions of the column oven were 90°C for 1 min (20°C/min) to 120°C (10°C/min) to 250°C for 10 min in DB-WAX, and 90°C for 1 min (20°C/min) to 150°C (10°C/min) to 300°C for 10 min in DB-17MS, respectively. The carrier gas was helium at a flow of 1 ml/min. The injection volumes were 2 µl. The MS was operated in the electron impact ionization (EI) mode using selected ion monitoring (SIM).

4 oligomeric phosphate esters were measured by LC-MS after the purification of these extracts with a Sep-Pak plus C18 (Waters). The LC-MS measurements were performed with Applied Biosystems API3200, Shimadzu LC-20A Prominence equipment, and an Inertsil ODS-3 column (50 mm x 2.1 mm i.d., particle size 3 µm, GL Sciences Inc., Japan). The mobile phase conditions were 50% H_2O/50% acetonitrile (ACN) followed by a linear gradient for 5 min to 10% H_2O/90% ACN, which was held for 17 min. The flow rate was 0.2 ml/min. The injection volumes were 20 µl. The MS was operated in the atmospheric pressure chemical ionization (APCI) positive ion mode using SIM.

Results and Discussion

Calculation of isomer contents in standards of TCIPP, CDP, and TCP

Standards of TCIPP, CDP, and TCP were consisted of some isomers. Fig.2 shows chromatograms of these compounds obtained by using GC-FID. All of the detected peaks were measured by GC-MS with scanning, and identified as their isomers and byproducts. The contents of these isomers and byproducts were calculated from the percentages of these peak areas which were averaged in three time of injection of GC-FID, and were multiplied with total concentration of their standard solution to use as the concentrations of their individual isomers in quantitative analysis.

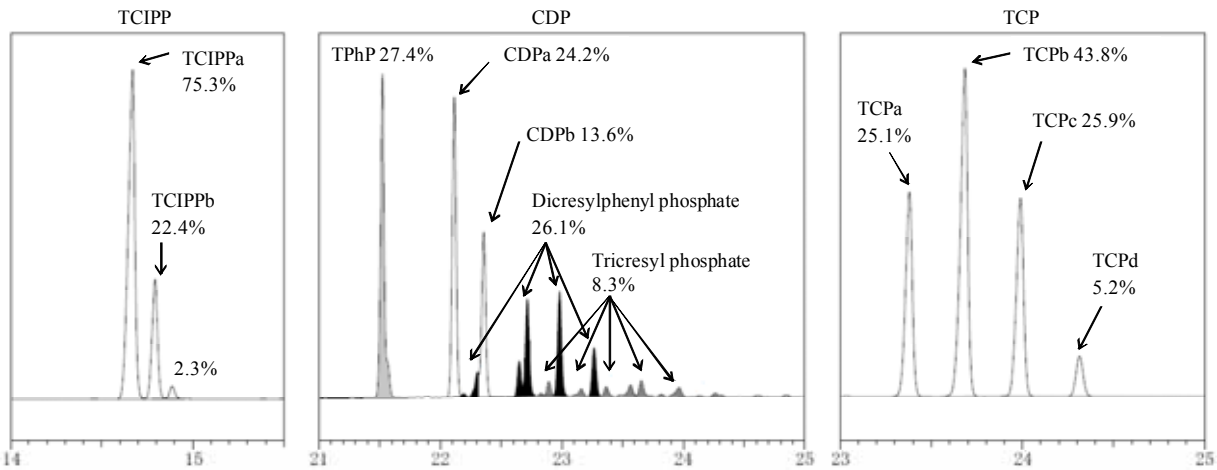

Fig. 2. The contents of the isomers and byproducts in standards of TCIPP, CDP, and TCP.

Calibration curves and detection limits

13 monomeric phosphate esters were calibrated in the concentration range of 2-50 ng/ml by GC-MS measurement used suitable surrogate substances. 4 oligomeric phosphate esters were calibrated in the concentration range of 0.5-50 ng/ml by LC-MS measurement. Calibration curves of analytes shown in Table 1 indicated a good linearity more than 0.997 of correlation coefficients. Instrument detection limits (IDLs) of analytes shown in Table 1 were 0.11-1.98 ng/mL, which were calculated from the standard deviation of the values that were practically measured 7 standards of concentration near the expected limit of detection for each compounds. Method detection limits (MDLs) of analytes shown in Table 1 were 0.32-3.3 ng/m^3 in indoor air, and 9-99 ng/g in house dust, which were estimated by multiplying the IDLs.

Table 1. Calibration curves and detection limits

Analytes		Surrogate substance		Calibration curve (y = ax + b)			IDL	MDL		Coefficient of variation
Name	Monitor ion m/z	Name	Monitor ion m/z	Slope (a)	Intercept (b)	Correlation coefficients (r)	(ng/mL)	Indoor air (ng/m^3)	House dust (ng/g)	(%)
TMP	110	TEP-d_{15}	167	6.363	0.003	1.000	1.27	2.11	63	5.6
TEP	155	TEP-d_{15}	167	1.535	0.004	1.000	0.70	1.16	35	3.3
TPrP	141	TBP-d_{27}	167	2.154	-0.018	0.999	0.92	1.54	46	4.5
TBP	155	TBP-d_{27}	167	1.442	-0.007	1.000	0.50	0.83	25	6.2
TCEP	249	TCEP-d_{12}	261	0.844	-0.007	0.998	0.19	0.32	9	3.0
TCIPPa	201	TCEP-d_{12}	261	0.899	-0.005	0.998	0.26	0.44	13	2.8
TCIPPb	201	TCEP-d_{12}	261	0.616	-0.002	0.998	0.88	1.47	44	9.9
ΣTCIPP	—	—	—	—	—	—	1.15	1.91	57	—
TEHP	99	TEHP-d_{51}	103	1.111	-0.010	0.999	0.25	0.42	13	1.3
TBEP	101	TEHP-d_{51}	103	0.092	-0.002	0.997	1.98	3.30	99	4.0
TDCPP	191	TPhP-d_{15}	339	0.622	-0.022	0.998	1.10	1.83	55	3.1
TPhP	326	TPhP-d_{15}	339	2.216	-0.031	0.997	0.26	0.44	13	2.7
CDPa	340	TPhP-d_{15}	339	2.272	0.000	0.999	0.15	0.25	7	7.6
CDPb	340	TPhP-d_{15}	339	2.334	-0.002	0.997	0.05	0.08	2	4.4
ΣCDP	—	—	—	—	—	—	0.20	0.33	10	—
TCPa	368	TCP-d_{21}	387	3.426	-0.008	0.998	0.12	0.20	6	6.4
TCPb	368	TCP-d_{21}	387	3.490	-0.013	0.998	0.15	0.25	7	4.4
TCPc	368	TCP-d_{21}	387	3.366	-0.011	0.997	0.17	0.28	8	8.3
TCPd	368	TCP-d_{21}	387	2.796	-0.004	0.998	0.11	0.18	5	4.8
ΣTCP	—	—	—	—	—	—	0.54	0.91	27	—
2,6-TXP	410	3,5-TXP-d_9	419	0.250	0.000	0.999	0.56	0.93	28	1.8
3,5-TXP	410	3,5-TXP-d_9	419	1.206	-0.004	1.000	0.31	0.52	16	4.3
RDP	575	—	—	11199	344	1.000	0.12	0.97	29	6.6
RDX	687	—	—	19431	-1372	1.000	0.14	1.17	35	6.9
BDP	693	—	—	8741	-394	1.000	0.11	0.89	27	5.3
CR-504L	573	—	—	2651	-174	1.000	0.24	1.99	60	6.1

Recoveries for indoor air

Recovery experiment was performed by spiking analytes to QFF and ventilating the Teflon holder for the QFF and Empore Disk C18 FF at a flow of 10 L/min for 4 h. Total recoveries of QFF and Empore Disk C18 FF were more than 89%, low-boiling OPCs such as TMP, TEP, TPrP, and TBP were passed to Empore Disk C18 FF, and other OPCs were left on QFF.

Determination in indoor air and house dust

In indoor air, TEP, TCEP, and TCIPP were detected with good recoveries of surrogate substances in the range of 78-120%. In house dust, most of the analytes were detected with good recoveries of surrogate substances in the range of 71-120%, especially, TCEP, TCIPP, TBEP, TCP, RDP, and CR-504L were contaminated in the level of μg/g orders. Fig. 3 shows the chromatograms of analytes in indoor air and house dust. The inference and failure of sensitivity derived from sample matrix were not observed in GC-MS and LC-MS measurement. These results suggested that this method allows analyzing the monomeric and oligomeric phosphate esters in indoor air and house dust.

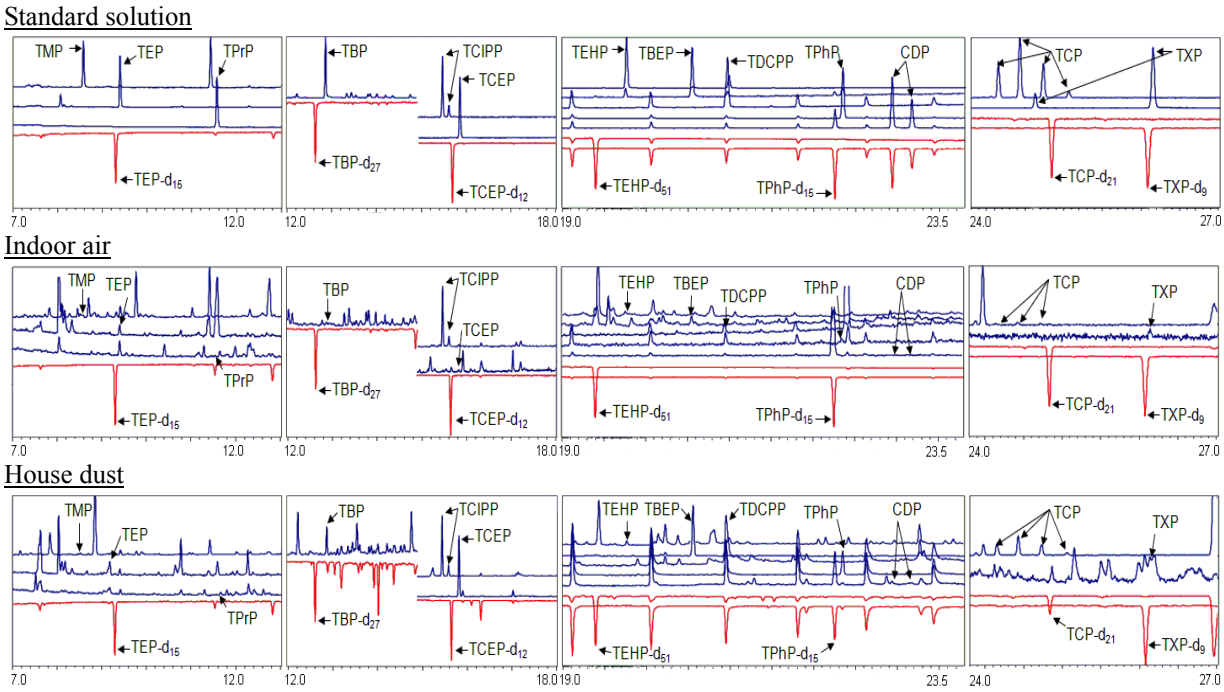

Fig. 3-1. Chromatograms of 13 monomeric phosphate esters in standard solution (upper), indoor air (middle), and house dust (lower). TMP, TEP, and TPrP were measured with DB-WAX column (30 m x 0.25 mm i.d., film thickness 0.25 μm), and TBP, TCEP, TCIPP, TEHP, TBEP, TDCPP, TPhP, CDP, TCP, and TXP were measured with DB-17MS column (30 m x 0.25 mm i.d., film thickness 0.25 μm).

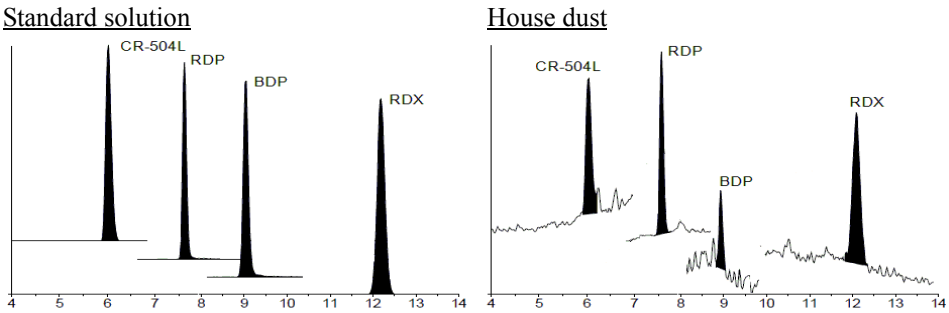

Fig. 3-2. Chromatograms of 4 oligomeric phosphate esters in standard solution (left) and house dust (right).