BROMINATED AND PHOSPHORUS COMPOUNDS IN TELEVISIONS AND A PERSONAL COMPUTER IN THE JAPANESE MARKET IN 2008

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Abstract
Brand-new electronic equipment including two liquid crystal display televisions and a laptop personal computer in the Japanese market in 2008 was investigated with respect to their content of brominated flame retardants (BFRs) and organophosphorus compounds (OPs). Although % order of bromine was detected in some components by X-ray fluorescence analysis, the bromine content cannot be fully explained by the respective BFRs including polybrominated diphenylethers, decabromodiphenyl ethane, tetrabromobisphenol A, polybromophenols, and hexabromocyclododecanes. This result indicates the use of alternative BFRs such as tetrabromobisphenol A epoxy oligomer and carbonate oligomer. Among 11 OPs analyzed, triphenylphosphate showed the highest concentrations in all the components analyzed, suggesting the use of condensed organophosphates as alternative flame retardants since they contain triphenylphosphate as impurity. Tripropylphosphate and tributyl tris(2-butoxyethyl)phosphate were not found in any samples, and trimethylphosphate and tris(1,3-dichloro-2-propyl)phosphate were in only some components with low concentrations. All the electronic equipment included in this study contained classical BFRs in inadequate amount for sufficient flame-retardant effect, implying incorporation of recycled plastic materials that contained certain BFRs of global concern. Since consumers are unable to protect themselves from hazards posed by toxic substances in articles at present, internationally standardized approach to information on chemicals in articles including recycled products should be developed.

Introduction
There is a growing interest of the potential human exposure to chemicals including brominated flame retardants (BFRs) contained in commonly used articles, such as electronic equipment, household items, and automobiles. In the absence of any internationally standardized approach to information on chemicals in articles, some jurisdictions have created information disclosure requirements. One of the innovative policies with international influence is RoHS (the Restriction of the use of certain Hazardous Substances in electrical and electronic equipment) Directive, which entered into force in 2006 in EU. The Directive bans the placing on the EU market of new electrical and electronic equipment containing more than agreed levels of hazardous metals (Pb, Hg, Cd, Cr^{6+}) and two kinds of BFRs including polybrominated diphenylethers (PBDEs) and polybrominated biphenyls. It is expected that an increasing number of phosphorus flame retardants (PFRs) and alternate BFRs will be globally consumed and consequently introduced into the environment due to the phase-out of PBDEs. In 2007, a new law REACH (Registration, Evaluation, Authorisation and Restriction of Chemicals) entered into force in EU and manufacturers and importers are required to gather information on the properties of their chemical substances and to register the information in a central database run by the European Chemicals Agency. Within the REACH framework, another BFR hexabromocyclododecanes (HBCDs) has been included in the list of Substances of Very High Concern (SVHC).

Although proper management of hazardous chemicals in the articles on the market is strongly required internationally, information on their chemical contents is scarcely reported so far. In this study, we investigated the contents of classical BFRs and organophosphorus compounds (OPs) in the major components of selected electronic equipment on the Japanese market to grasp current situation of their usage.

Materials and Methods
In February 2008, a screening survey was carried out using a handheld X-ray fluorescence (XRF) analyzer (Innov-X Systems, Inc., MA, US) at an electronic appliance store in Japan to obtain information on the substances contained in housing of the latest electronic equipment. Based on bromine (Br) and phosphorus (P) contents, two liquid crystal display televisions (LCD TV-1, -2) and a laptop personal computer (laptop PC)

produced by leading Japanese companies were selected as target articles of this study. They were dismantled manually upon purchase and element content at several spots of each component surface was determined by the handheld XRF analyzer. For LCD TVs, front and rear covers, printed circuit boards (PC boards) for power supply and fluorescent tube, the composite of remaining PC boards (other PC boards), and outermost part of the LCD panel were selected for further chemical analysis. PC board for power supply and fluorescent tube of LCD TV-1 was separated whereas those of LCD TV-2 were integrated. From the laptop PC, bottom of chassis, keyboard top, PC board, cooling fan, speaker, AC adapter, and outermost part of the LCD panel were selected. All the PC boards found in the laptop PC were combined into one composite sample. Since cooling fan and speaker were too small to employ chemical analysis independently, these two components were combined for further analysis. Surface projections on all the PC boards were removed as much as possible. Except PC boards, plastic material of each component was used for chemical analysis.

Table 1. Target compounds of this study

Compound	Abbreviation
polybrominated diphenylethers	PBDEs
decabromodipheny ethane	DeBDethane
tetrabromobisphenol A	TBBPA
polybromophenols	PBPhs
hexabromocyclododecanes	HBCDs
trimethylphosphate	TMP
triethylphosphate	TEP
tripropylphosphate	TPrP
tributyl phosphate	TBP
tris(2-chloroisopropyl)phosphate	TClPP
tris(2-chloroethyl)phosphate	TCEP
tris(2-butoxyethyl)phosphate	TBEP
tris(1,3-dichloro-2-propyl)phosphate	TDCPP
tris(2-ethylhexyl)phosphate	TEHP
triphenylphosphate	TPhP
tricresyl phosphate	TCP

Selected components were crushed and homogenized into small pieces, and then, further pulverized to fine powder prior to the ultrasonic extraction with toluene. Hexane was added to the crude extracts to precipitate the dissolved polymer matrix. To analyze 5 BFRs and 11 OPs listed in Table 1, the extracts were divided into four aliquots, which were fortified, respectively, with ^{13}C- or deuterium-labeled internal standards. After sufficient clean-up, PBDEs, DeBDethane, TBBPA, PBPhs, and OPs were determined using a HRGC/HRMS, whereas HBCDs were determined using a LC/MS.

Results and Discussion

Maximum concentrations of Br detected by XRF analysis in each component are shown in Table 2–4. In contrast to Br, the handheld XRF analyzer used in this study has a very poor sensitivity to detect light element including P. Therefore, this testing device was tentatively introduced to the present survey as a rough guide for determining whether an article contains very high level of OPs. LCD TV-1 was found to contain more than 10% of Br in its covers: some sort of BFRs is used in this product. On the other hand, LCD TV-2 and the laptop PC were selected for this study since OPs were suggested to be used in their housing instead of BFRs. As a result of further analysis by mass spectrometry, BFRs and OPs were detected in all the three articles investigated (Table 2–4). Although some components contained % order of Br, the Br content cannot be fully explained by the respective BFRs analyzed, indicating the use of alternative BFRs. Generally, HBCDs were the most minor BFRs in these products, confirming that this BFR is not primarily added in rigid plastic, but in polystyrene foams for thermal insulation in the building industry and in upholstery textiles[1]. Among 11 OPs analyzed, TPhP showed the highest concentrations in all the components analyzed. TPrP and TBEP were not found in any samples, and TMP and TDCPP were in only some components of the laptop PC with low concentrations. Concentration profile of OPs in this study was apparently different from those found in floor dust of a hotel in Japan reported recently: TBEP was the predominant compound[2], indicating the difference in potential sources.

Among 5 BFRs analyzed, concentration of DeBDethane was the highest in rear and front covers of LCD TV-1, followed by PBDEs and PBPhs (Table 2). It was, however, far lower level than general content of flame retardants intentionally added to flammable polymer, indicating the use of BFRs other than 5 formulations analyzed in this study. As 2,4,6-triBPh was the predominant isomer of PBPhs in casing samples of LCD TV-1 contributing approximately 90% of the total PBPhs (data not shown), the use of ‘reactive’ BFRs such as TBBPA

epoxy oligomer and carbonate oligomer using 2,4,6-triBPh as ends-caps was suggested. 2,4,6-triBPh is used primarily as the intermediate for the products such as ends-caps for brominated epoxy resins made from TBBPA and 1,2-bis(2,4,6-tribromphenoxy)ethane[3]. Actually, 2,4,6-triBPh has so far been detected at concentrations up to 0.05 weight % in these high molecular BFR formulations[4]. Therefore, if 10 weight % of the reactive BFR above is added to polymer, roughly 50,000 ng/g of 2,4,6-triBPh can be included as impurity and/or unreacted element.

The use of high molecular BFRs including TBBPA epoxy oligomer and carbonate oligomer were also presumed for the composite sample of cooling fan and speaker of the laptop PC. In this sample, TBBPA shows the highest concentration reaching approximately 1%, followed by PBPhs and DeBDethane (Table 4). Considering the fact that Br content of this sample was about 10%, the primarily use of BFRs other than those analyzed in this study was conceivable. As described above, TBBPA is used also as raw material of reactive BFRs. Thus, TBBPA detected in this sample are thought to be the impurity and/or unreacted element of the raw materials. For AC adapter, only small amount of BFRs analyzed was found, indicating that we did not capture the specific flame retardant actually added to this component.

In stark contrast to LCD TV-1, Br concentrations in covers of LCD TV-2 were lower than detection limit and TPhP was the predominant compound detected (Table 3), indicating some sort of PFRs was used in this article. As in the case of LCD TV-2, TPhP concentration was also the highest in the bottom of chassis and keyboard top of the laptop PC (Table 4). However, it is quite unlikely that TPhP itself was used as flame retardant of these individual components since % order concentrations of OPs have generally been added to polymer to achieve sufficient flame retardancy[5]. It is highly possible that 'condensed type' PFRs such as resorcinol bis(diphenylphosphate) (RDP) and bisphenol A diphoshate (BDP) were applied to these articles, since they contain approximately 3–5 weight % of TPhP as impurity[6]. Condensed type PFRs are high-molecular-weight compounds with extremely low volatility compared to their monomer, TPhP. From the viewpoint of reductions in indoor emissions of flame retardants from the articles, the consumptions of condensed type PFRs have risen dramatically over the past decade in Japan[5].

Since a PC board is assembled from numerous plastic and metallic parts, it is not possible to determine concentrations of flame retardants only in the polymer used for laminating the board. On that basis, contrary to expectation, TPhP and TCP were the two dominant compounds detected in almost all PC boards of two LCD TVs investigated (Table 2, 3). Remarkably high level of BFRs was not found. Since organophosphates are easy to evaporate and not stable to hydrolysis, it is not common to use them for the components like PC boards which will be subjected to high temperature. However, the result of this study implies that organophosphates are used also in PC boards as flame retardants and/or plasticizers to some extent. Condensed type PFRs might be used as well because their stability has been greatly improved. On the other hand, only small amount of OPs were found in other PC boards of LCD TV-2 (Table 3) and PC boards of the laptop PC (Table 4).

As for LCD panels, TPhP was the predominant compound detected, with concentrations ranging from 0.12 to 0.26% (Table 2–4). In this particular case, detected TPhP is thought to be used not as a flame retardant, but as a plasticizer of triacetyl cellulose (TAC) film, which is widely used as a protective film for polarizers in a LCD. It is known that TAC film contains 10–20% of TPhP as plasticizer. The outermost part of the LCD panel analyzed in this study were made up of several layers of sheets glued together, which means that one of them will be the TAC film.

In conclusion, the result of this study implies that the latest electronic equipment on the Japanese market are flame retarded by reactive BFRs and/or condensed type PFRs as alternatives to chemicals of global concern. Further risk assessment is required to answer the recurring question whether the alternative flame retardants are safer than classical ones from the viewpoint of human and environmental health and safety. Besides, we should pay careful attention to the fact that all the samples analyzed in this study also contained classical BFRs in inadequate amount for sufficient flame-retardant effect. A plausible explanation is that some components were manufactured using recycled plastic materials that contained certain BFRs. There is also a possibility that the articles were unintentionally contaminated by those BFRs by sharing the manufacturing lines. Since consumers are unable to protect themselves from hazards posed by toxic substances in articles at present, internationally

standardized approach to information on chemicals in articles including recycled products should also be developed.

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Table 2. Concentration (ng/g) of brominated and phosphorus compounds in LCD TV-1

	Rear cover	Front cover	Power board	PC board for fluorescent	Other PC boards	LCD panel
PBDEs	14,000	14,000	15	54	59	2.4
DeBDethane	130,000	92,000	1,100	770	36	na
TBBPA	68	92	90	890	87	7.3
PBPhs	5,700	4,600	980	1,200	730	33
HBCDs	< 0.5	6.1	130	680	< 0.5	1.9
Total Br (XRF)	140,000,000	130,000,000	130,000	23,000,000	24,000,000	< 18,000
TMP	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
TEP	0.50	3.0	3.6	1.1	0.70	6.3
TPrP	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
TBP	16	11	3.4	1.8	2.1	2.5
TClPP	10	14	52	16	23	4.0
TCEP	7.0	4.0	< 4	4.0	9.0	< 4
TBEP	< 80	< 80	< 80	< 80	< 80	< 80
TDCPP	< 2	< 2	< 2	< 2	< 2	< 2
TEHP	2.7	17	< 0.9	5.7	< 0.9	< 0.9
TPhP	1,100	2,400	6,700,000	320,000	1,600,000	1,200,000
TCP	180	370	4,500,000	140,000	480	54

na: no data available

Table 3. Concentration (ng/g) of brominated and phosphorus compounds in LCD TV-2

	Rear cover	Front cover	PC board for power supply and fluorescent	Other PC boards	LCD panel
PBDEs	32	540	13	45	5.4
DeBDethane	na	na	2,400	380	na
TBBPA	15	21	840	74	8.7
PBPhs	41	65	250	120	4.8
HBCDs	53	40	400	3.9	< 0.5
Total Br (XRF)	< 1,000	< 1,000	42,000,000	90,000,000	< 20,000
TMP	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3
TEP	0.40	0.40	190	0.40	0.30
TPrP	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
TBP	2.1	2.3	7.7	1.9	1.5
TClPP	4.0	9.0	5.5	26	4.0
TCEP	< 4	< 4	5.5	7.0	< 4
TBEP	< 80	< 80	< 80	< 80	< 80
TDCPP	< 2	< 2	< 2	< 2	< 2
TEHP	< 0.9	80	< 0.9	< 0.9	< 0.9
TPhP	600,000	940,000	14,000,000	870	1,200,000
TCP	47	140	84,000	72	110

Table 4. Concentration (ng/g) of brominated and phosphorus compounds in a laptop PC

	Chassis	Keyboard top	PC boards	Cooling fan and speaker	AC adapter	LCD panel
PBDEs	68	130	70	4,800	6.9	6.7
DeBDethane	670	na	37	19,000	na	na
TBBPA	2,700	1,400	800	9,500,000	81	110
PBPhs	600	260	180	110,000	44	32
HBCDs	210	4.4	1.4	610	< 0.5	< 0.5
Total Br (XRF)	490,000	< 2,000	80,000,000	95,000,000	4,900,000	23,000
TMP	< 0.3	0.70	< 0.3	0.50	< 0.3	< 0.3
TEP	6.0	17	56	30	1.1	13
TPrP	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5
TBP	1.6	1.8	4.4	1.8	1.3	1.2
TClPP	100	11	34	4.0	150	12
TCEP	16	< 4	14	120	< 4	< 4
TBEP	< 80	< 80	< 80	< 80	< 80	< 80
TDCPP	< 2	< 2	9.0	14	35	< 2
TEHP	130	190	< 0.9	26	1,300	< 0.9
TPhP	170,000	500,000	560	42,000	1,800	2,600,000
TCP	390	28	43	3,600	17	130