

Simultaneous Analytical Method for Brominated and Phosphorus Flame Retardants in Human Sample

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Introduction

Many consumer products in modern life contain brominated and organo phosphorus flame-retardants (BFRs and PFRs) for the purpose of fire protection. Polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol A (TBBPA) are used in large quantities as BFR additives in television sets, computers, radios, textiles, and in synthetic building materials and automobiles. Prior to 1990, the primary BFRs in Japan were PBDEs. These PBDEs are found in the human tissues and environment. PBDEs have high accumulation, and the metabolism of PBDEs show thyroid hormone disrupting effect. From these things, the use of PBDEs was limited in Stockholm Convention on Persistent Organic Pollutants and Act on the Evaluation of Chemical Substances and Regulation of their Manufacture in Japan. With the phasing out of PBDEs, TBBPA is used as replacements. TBBPA is a common reactive BFR for ABS and epoxy resins due to its low toxicity and cost. However, TBBPA is likely to contaminate the environment during its production, use, and disposal. In fact, TBBPA has been detected in river sediment¹. Limited information concerning the toxicological impact of TBBPA is available. *In vitro* studies have reported that TBBPA induces neurotoxicity², and estrogenic activity³. Recently, TBBPA has been classified as Type 2A Carcinogen by the IARC⁴.

On the other hand, usage of PFRs increase rapidly after 1998 (Table 1). Although acute toxicity of PFRs is low, in recent years tris(dichloroisopropyl) phosphate (TDCIPP) showed disruption of sex hormone balance through several mechanisms including alterations of steroidogenesis or estrogen metabolism.

In Dioxin 2016, we have already reported that TBBPA contamination levels in human breast milk⁵. As described above with regulation of BFRs, it is important to monitor of PFRs pollution. However, because a method to analyze all at once is not developed with these flame retardants, we think that it was obstruction to elucidate of human contamination.

In this paper, we describe development of analytical method for brominated and phosphorus flame retardant.

Table 1 Demands (ton) for phosphorus flame retardants in the last three decade

Year	Phosphate triester ¹⁾	Chlorinated phosphate triester	Total
1986	4,000	2,900	6,900
1988	4,200	3,000	7,200
1990	4,400	3,000	7,400
1992	4,400	3,100	7,500
1994	4,400	3,100	7,500
1996	4,400	3,300	7,700
1997	4,600	3,100	7,700
1998	22,000	4,000	26,000
2000	22,000	4,000	26,000
2002	20,000	4,000	24,000
2004	24,000	4,000	28,000
2006	24,000	4,000	28,000
2008	20,000	4,000	24,000
2010	20,000	2,500	22,500
2012	20,000	2,500	22,500
2014	20,000	2,500	22,500

1) Among phosphorus flame retardants, triphenyl phosphate and tris(dichloroisopropyl) phosphate are main phosphorus flame retardants.

Examinations

1. Recovery test of PBDE and PFRs using solid phase extraction (HLB cartridge, Waters, Tokyo, Japan)
2. Clean-up of human breast milk with partitioning of acetonitrile and n-hexane
3. Calibration curve and limit of detection (LOD) of PFRs

Results and discussion

1. Recovery test

We measured recovery of labelled flame retardants when they were added ¹³C-PBDE and d-PFRs in human breast milk. As a result, recovery of ¹³C-Tri-DeBDE and d-PFRs were ranged from 64-116 and 74-89%, respectively. D-PFRs were d-triethyl phosphate, d-tripropyl phosphate, d-tributyl phosphate, d-triphenyl phosphate, d-tris(2-chloroisopropyl) phosphate, d-tris(1,3-dichloro-2-propyl) phosphate.

2. Clean-up

After solid-phase extraction with HLB cartridge, we measured PFRs using GC-MS. It was cleared that difficult to determine by the interference such as oil and fat (Fig 1-1).

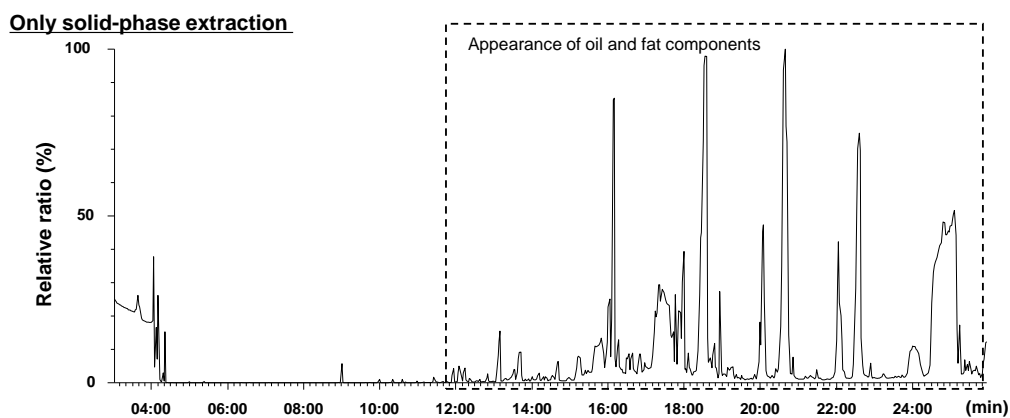


Fig. 1-1 Total ion chromatogram of PFRs measurement in human breast milk after solid-phase extraction

Therefore performed the partition with acetonitrile and hexane after solid-phase extraction as clean-up of oil and fat. As a results, quantitative analysis of PFRs was enabled (Fig. 1-2).

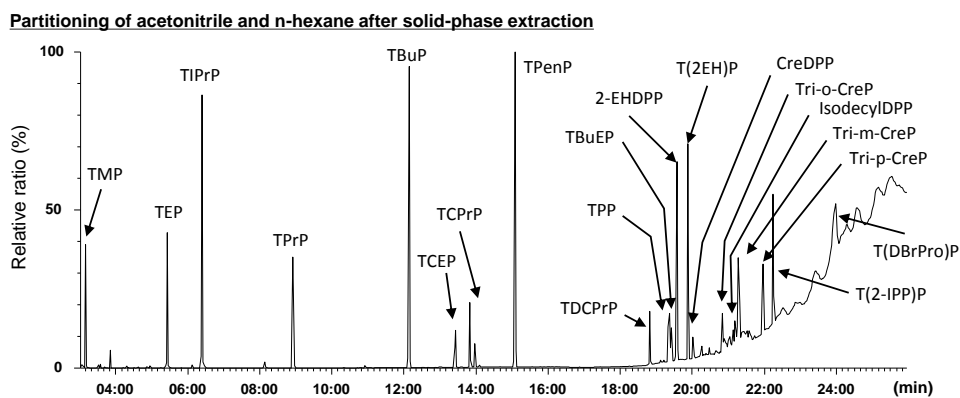


Fig. 1-2 Total ion chromatogram of PFRs measurement in human breast milk after partitioning with acetonitrile and n-hexane

3. Calibration curve and LOD of PFRs

We made a linear regression curve about tributyl phosphate, triphenyl phosphate and tris(1,3-dichloro-2-propyl) phosphate. As shown in Fig. 2, these PFRs showed straightness in the range of 0.1 – 100 ng/ml. Their coefficient of correlation was higher than 0.9995. Moreover, their LOD were 0.012 – 0.3 ng/g lipid.

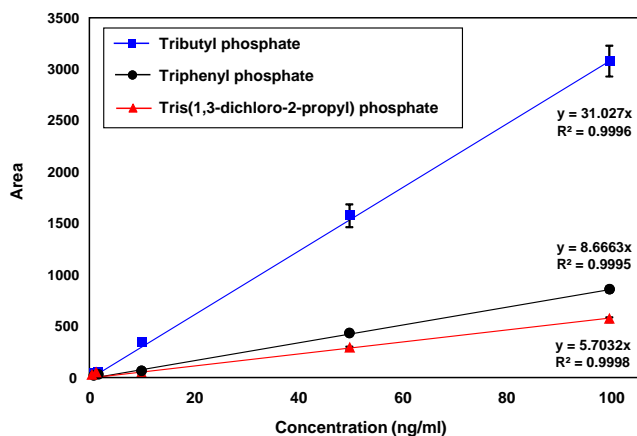


Fig. 2 Calibration curve of major phosphorus flame retardants

From these results, we developed a new method for BFRs and PFRs combined with solid-phase extraction and partitioning with acetonitrile and n-hexane.

Acknowledgements

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