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Recent advances in the analysis of TBBPA/TBBPS, TBBPA/TBBPS derivatives and their transformation products



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ABSTRACT

Tetrabromobisphenol A (TBBPA) is the most widely used brominated flame retardant. TBBPA and its alternative, tetrabromobisphenol S (TBBPS), are the reactive chemicals used to produce TBBPA/S derivatives. The manufacturing and application of TBBPA/S derivatives may result in their accumulation in environmental compartments and may cause risks to environmental safety and human health. To investigate the occurrence and transformation products of TBBPA/S and TBBPA/S derivatives, it is imperative to develop effective sample preparation and sensitive analytical methods for various environmental matrices. In this paper, we summarize the techniques for analysis of TBBPA/S and their derivatives. We also critically review methodologies for the identification of unknown metabolites transformed from these chemicals. In the perspective section, we discuss trends in analytical strategies for studying emerging TBBPA/S derivatives.

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Abbreviations: APPI, atmospheric pressure photoionization; APCI, atmospheric pressure chemical ionization; ASE, accelerated solvent extraction; ELISA, enzyme-linked immunosorbent assay; BFRs, brominated flame retardants; DSPE, dispersive solid-phase extraction; DLLME, dispersive liquid-liquid microextraction; ECF, electrochemical fluorination; EESI, extractive electrospray ionization; EI, electron impact; ESI, electrospray ionization; FT, fluorotelomer; GC-MS, gas chromatography—mass spectrometry; HRMS, high-resolution mass spectrometry; GPC, gel permeation chromatography; IDL, instrument detection limit; ITMS, ion trap mass spectrometer; LC-MS/MS, liquid chromatography coupled with tandem mass spectrometry; LLE, liquid-liquid extraction; LSC, liquid scintillation counting; MDLs, method detection limits; MCFs, mesoporous cellular foams; MS, mass spectrometry; MRM, multiple-reaction monitoring; MSPE, magnetic solid-phase extraction; MTBE, methyl tert-butyl ether; NCI, negative chemical ionization; MDLs, method detection limits; PSA, primary—secondary amine; QqQ-MS, triple-quadrupole mass spectrometry; QSAR, quantitative structure–activity relationship; SERS, surface-enhanced Raman scattering; SPE, solid-phase extraction; TOF, time of flight; TRFIA, time-resolved fluoroimmunoassay.

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1. Introduction

The most widely used brominated flame retardant (BFR), tetrabromobisphenol A (TBBPA), is frequently being used in plastics, textiles, and electronics [1]. TBBPA and its alternative, tetrabromobisphenol S (TBBPS), are the reactive chemicals used to produce TBBPA/S derivatives, via modification of the TBBPA/S hydroxyl groups. These derivatives can be added in polymer products or selected as precursor compounds for a series of other TBBPA-based polymers [2,3]. The contamination of TBBPA/S and TBBPA/S

derivatives in the environmental matrices leads to potential environmental and health risks. Studies on toxicity evaluation have indicated the potential adverse effects of these chemicals on mammals and aquatic organisms [4], while the transformation of TBBPA in the environment may alter their potential biological effects due to their transformation products [5,6]. TBBPA/S derivatives discussed in the current review were summarized in Fig. 1. The first group of TBBPA derivatives developed for industrial application was synthesized using TBBPA/S as a raw material with the two phenolic hydroxyl groups modified. Here, these chemicals are referred to

TBBPA/S derivatives and intermediate products	TBBPA/S byproducts	Important products of TBBPA
Br Br Br TBBPA BGE	Br Br Br TBBPA MGE	Br Br Br TBBPA BME
Br OH O Br Br TBBPA BHEE	Br OH HO Br Br TBBPA MHEE	Br Br OH Br TBBPA MME
Br B	Br Br Br TBBPA MAE Br Br HO Br	Br Br OH Br NO ₂ NTriBBPA Br OH HO OH Br Br
Br TBBPA BDBPE	Br Br Br TBBPA MBAE	HTriBBPA Br HO————————————————————————————————————
Br O Br O Br TBBPS BAE	Br O Br O Br TBBPS MAE	Вг Вг ОН
Br O Br O Br Br TBBPS BDBPE	Br O Br O Br O Br TBBPS MDBPE	HO————————————————————————————————————
	Br O Br O Br O Br TBBPS MBAE	HO——————OH Br MBBPA

Fig. 1. Chemical structures of important TBBPA/S derivatives.

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