Occurrence and Fate of Alternative Flame Retardants in the Environment

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3.1: Analysis of two alternative organophosphorus flame retardants in electronic and plastic consumer products: resorcinol bis-(diphenylphosphate) (PBDPP) and bisphenol A bis (diphenylphosphate) (BPA-BDPP)

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Abstract

Following the phase-out of polybrominated diphenyl ethers (PBDEs), organophosphorus flame retardants (PFRs) are increasingly used as alternative flame retardants in many products. Data on the presence of two alternative PFRs in consumer products, resorcinol bis (diphenylphosphate) (PBDPP or RDP) and bisphenol A bis (diphenylphosphate) (BPA-BDPP or BDP) is still scarce or non-existing. In this study we propose a simple extraction method and analysis by liquid chromatography-atmospheric pressure chemical ionization (APCI) coupled to a high resolution time-of-flight mass spectrometry (TOF) for plastic consumer products. Detection limits were low enough for trace quantitation in plastic or electronic samples (0.001 and 0.002 % w/w for PBDPP and BPA-BDPP, respectively). The APCI source provided better sensitivity and matrix effects than the commonly used ESI source for the analysis of these PFRs. Both PBDPP and BPA-BDPP were detected in 7 of the 12 products purchased in 2012 (at 0.002-0.3 % w/w for PBDPP and 0.02-0.18 % w/w for BPA-BDPP) while only PBDPP was found in 4 of the 13 products purchased before 2006 (0.005-7.8 % w/w). In newly purchased products, PBDPP, BPA-BDPP and tris(phenyl) phosphate (TPHP) were the most frequently detected PFRs. These results support the recent findings of our research group about high concentration levels of PBDPP and BPA-BDPP up to 0.5-1 mg g^{-1} in house dust collected on electronic equipment and highlights the need for further research on these two novel PFRs.

Introduction

Brominated flame retardants (BFRs) are widely used in common materials and products such as plastics, electronic equipment, textile, furniture and building materials in order to prevent fire (De Wit, 2002; Birnbaum et al., 2004). Many BFRs are widespread in the environment and present in human tissues and blood (De Wit, 2002; Law et al. 2006; Besis et al., 2012; Wan-Li et al., 2013) and have been reported to cause neurotoxicity, thyroid hormone effects and certain morphological effects in the liver and kidney (Darnerud et al., 2003).

In order to protect the environment and human health, the commercial formulations of polybrominated diphenyl ethers (PBDEs), have been banned or phased out by both EU (Directives 2003/11/EC and 2002/95/EC and European Court of Justice on 9.5.2008) and US regulations (Betts, 2008 and Kemmlein et al., 2009), which resulted in increased application of alternative flame retardants in order to comply with flammability standards in consumer products.

One such alternative class of flame retardants are the organophosphorus flame retardants (PFRs). Stapleton et al. (2012) identified tris(1,3-dichloroisopropyl) phosphate (TDCIPP) and components associated with Firemaster550, a mixture containing 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EH-TBB), bis (2-ethylhexyl) 2,3,4,5- tetrabromophthalate (BEH-TEBP) and tris(phenyl) phosphate (TPHP), as major flame retardants in polyurethane foam from couches purchased after the phase-out of Penta-BDE in 2005. Two chlorinated PFRs not previously reported in the environment, V6 and a

derivative that contains tris(2-chloroethyl) phosphate (TCEP) as an impurity, were identified in baby products and dust coming from polyurethane foam (Fang et al., 2012; Stapleton et al. 2013). In a recent study on dust collected in houses from California by Dodson et al. (2012), the concentration of carcinogenic chlorinated organophosphorus compounds (TCEP and TDCIPP) were found up to 0.01% w/w in dust, values higher than those previously reported in the USA. In the same study, tris (2,3-dibromopropyl) phosphate (TDBPP), or brominated "Tris" was also reported for the first time in house dust and concentrations of Firemaster 550 components were higher in 2011 than 2006. This compound was banned in children's sleepwear due to its carcinogenicity.

In contrast to these chemicals, few data are available for two other novel organophosphorus flame retardants, resorcinol bis (diphenylphosphate) (PBDPP or RDP) and bisphenol A bis (diphenylphosphate) (BPA-BDPP or BDP). PBDPP and BPA-BDPP can be used as an alternative for decabromodiphenyl ether (Deca-BDE) in TV/flat screen housings and other electronic consumer products (Lowell Center for Sustainable Production, 2005) and they are applied in a variety of polymers. PBDPP is used in acrylonitrile butadiene styrene (ABS), polycarbonate (PC)/ABS, poly(p-phenylene) oxide (PPO)/ high impact polystyrene (HIPS) and BPA-BDPP in HIPS, PC, PPO and PC/ABS (Roth et al., 2012). There are few toxicity data for PBDPP and BPA-BDPP, although some aquatic toxicity studies in the literature show varying results with moderate-low and high-low toxicity, respectively (Waaijers et al., 2013). This variation may be due to the presence of tris(phenyl) phosphate (TPHP) as a by-product in the PBDPP and BPA-BDPP technical products (up to 5%); TPHP is known to be toxic to aquatic organisms (EC10 = 0.037 mg/L for Oncorhynchus mykiss) (Waaijers et al., 2013). Levels of PBDPP and BPA-BDPP have been recently reported by our research group in dust samples from the Netherlands, Greece and Sweden. High concentrations were found in dust collected on electronic equipment (<0.1-1300 µg/g for BPA-BDPP and <0.04-520 µg/g for PBDPP), while lower levels were measured further away from the electronics (Brandsma et al., 2013)

To the best of our knowledge the only data on PBDPP and BPA-BDPP are from Roth et al. (2012), who reported a method based on ultrasonic supported extraction and precipitation for the analysis of PFRs in polymer parts of electrical and electronic devices by gas chromatography-quadrupole mass spectrometry (GC-q-MS) analysis. PBDPP was found at 21.4-17.4% w/w in PPO/HIPs polymers and at 0.18 % w/w in PC polymer. BPA-BDPP was found at 3.3- 7.0% w/w in PC and at 13.2% w/w in ABS/PC polymer in samples obtained from actual and second-hand equipment as well as waste devices gathered from collection stations and recycling plants (Roth et al., 2012). In the current study we present a sensitive and selective liquid extraction followed by LC-APCI(+)-HRTOF-MS method for the quantification of PBDPP and BPA-BDPP in a variety of plastic products commonly found in the indoor environment, making them a potential route via which human exposure can occur.
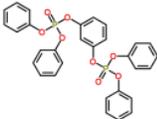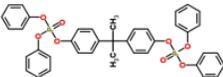
Material and methods

Chemicals and reagents

All solvents were of analytical grade and used as supplied. Dichloromethane and methanol were from Promochem, (Wesel, Germany) and toluene from Fisher Scientific (Loughborough, UK). Milli-Q water was obtained from ultrapure water purification Q-Pod system (Millipore, Bedford, USA). PBDPP (Fyrolflex RDP, technical grade, 95.5% purity) and and BPA-BDPP (Fyrolflex BDP, technical Grade, 96.5% purity) were obtained from ICL (Amsterdam, the Netherlands). The structure and physico-chemical properties of the analytes are given in Table 1.

The internal MS calibration was made with an APCI-TOF tuning mix provided by Supelco (Bellefonte, PA, USA). MS internal calibration in each run was performed by infusing the calibration solution into the source within the first minute of the chromatogram by using a syringe pump (as designed by the supplier of the instrument). The internal calibration was performed by enhanced quadratic mode, being values below 5 ppm mass error considered acceptable.

Table 1. Physico-chemical information of PBDPP and BPA-BDPP.

Abbreviation	CAS number	Chemical name	Structure	Formula	[a]LogKow	[a]Vapour pressure (Pa)
PBDPP	57583-54-7	Resorcinol bis(biphenylphosphate)		$C_{30}H_{24}O_8P_2$	7.08	5.01E-11
BPA-BDPP	5945-33-5	Bisphenol A bis(bisphenylphosphate)		$C_{39}H_{34}O_8P_2$	8.29	1.97E-15

[a]Values reported by Bergman et al., 2012

Apparatus

A microTOF II with resolution >16,500 FWHM equipped with an LC-APCI II source (Bruker Daltonics, Bremen, Germany) was used as detector. An electrospray ionization (ESI) source was also used for comparison. The LC system was an Agilent 1220 Infinity LC. A Kinetex core-shell LC C18 column (2.1 mm x 100mm x 2.6 μm) was obtained from Phenomenex (Torrance, California).

The software data analysis 4.0 and compass quant analysis from Bruker Daltonics (Bremen, Germany) was used for data processing (confirmation and quantitation). MS confirmation of the presence of analytes was based on mSigma (match factor between the measured isotopic pattern and the theoretical pattern for a given formula) and mass accuracy. Values of less than 5 ppm of mass error and less than 100 of mSigma were considered acceptable for positive confirmation (mSigma <100 acceptable, <50 good and <25 excellent).

Sample extraction and analysis

A total of 12 plastic products recently purchased (including powerboards, televisions, adaptors, toys, a plastic adorn and a heat sealer) and 13 old plastic products purchased before 2006 (including televisions, scanners, printers and a computer monitor) obtained from a recycling park in Amsterdam were analyzed.

Small pieces of the samples (~50 mg, obtained with a small cutter) were extracted with 20 mL of dichloromethane (shaking for 24h and sonication for 10 min) and then 10-100 times diluted with methanol as required. Extracts were ultracentrifuged in Eppendorf microtubes (10.000 rpm, 5 min) for the precipitation of minor remaining solids and aliquots of 2.5 μL were finally injected in the LC system. The LC mobile phase consisted of water (A) and methanol (B) both containing 0.25% v/v formic acid at a flow rate of 0.3 mL min^{-1}. The gradient was as follows: 60% B for 1.5 min and then to 93.5% B in 17 min, then up to 100% B and hold for 5 min (for removal of highly hydrophobic compounds) and finally re-conditioning for 8 min.

Calibration standards were prepared in methanol at concentrations within the range 5-1000 ng mL^{-1}.

Results and discussion

LC-HR-TOF-MS parameters optimization

PBDPP and BPA-BDPP could be analyzed by both ESI and APCI sources operating in positive mode, with [M+H] as the major ion. It is well-known than the APCI source is more suitable for the analysis of non-polar compounds than the ESI source and the sensitivity was indeed around 1.5 and 1.7 times higher in the APCI mode for PBDPP and BPA-BDPP, respectively.

MS-TOF parameters (mainly capillary exit and skimmer1: hexapole RF; transfer time and puls storage time) are dependent on the *m/z* value and influence sensitivity. These parameters were optimized for the *m/z* of interest in the range 550-700 *m/z* (see Table 2). Although it was not the focus of this study, the presence of other PFRs in the samples was investigated for discussion of the results. A number of other PFRs and plasticizers, namely tris(butyl) phosphate (TNBP); tris(2-chloroisopropyl) phosphate (TCIPP); tris(2-butoxyethyl) phosphate (TBOEP); 2-ethylhexyldiphenyl phosphate (EHDP); 2-ethylhexyl phosphate (TEHP); and tris(phenyl) phosphate (TPHP); tris(methylphenyl) phosphate

(TMPP), tris(isobutyl) phosphate (TIBP), tris(2-chloroethyl) phosphate (TCEP) and 3,4:5,6-dibenzo-2H-1,2-oxaphosphorin-2-oxide (DOPO) could also be analyzed by LC-APCI(+)-MS, also with [M+H] as the major ion, except for EHDP for which the fragment $[M-C_8H_{17}+H_2]$ was the main ion. The structure and mass accurate values of these compounds can be found in Figure S-1 of the Supplementary Information. The use of LC-APCI-MS for the analysis of PFRs has been hardly reported. Regarding the study of Amini and Crescenzi (2003), the APCI(+) ionization of organophosphorus triesters was much less affected by the matrix than the ESI (+) ionization, and the signal was significantly more stable. However, in this study ESI provided better sensitivity for most of the compounds (5-30 times better). APCI ionization is proposed for the first time as an alternative for the ESI ionization of PBDPP BPA-BDPP, for which not only less matrix effects (ion suppression or enhancement) but even a slightly better sensitivity was obtained due to the suitability of this source for highly non polar compounds.

Source parameters were optimized by injecting into the source a solution of PBDPP and BPA-BDPP in methanol at a concentration of around 0.5 mg mL^{-1} by using a syringe pump (optimal values are given in Table 2). The vaporizer gas temperature was set at 240 ºC to prevent thermal degradation of the analytes that occurred above 280º C (the signal being completely lost).

Table 2. APCI source and MS parameters for the analysis of PBDPP and BPA-BDPP.

APCI source	HR-TOFMS
Capillary -1000 V	Capillary exit: ±100 V
End plate offset -500	Skimmer1: ±33 V
Corona +5000 nA	Hexapole 1: 23 V
Dry gas 2 L min^{-1}	Hexapole RF: 200 V
Nebulizer 2 bar	Transfer time: 70
Dry Heater 220 ^{o}C	Puls storage time: 15
Vaporizer temperature at 240°C	

Regarding the LC chromatographic separation, it is worth mentioning that a significant improvement in peak shape was observed when using the core-shell as used in this article in comparison with an equivalent fully porous particles C18 column.

Analytical performance of the method

The extraction method was validated by analyzing two polymer materials made of acrylonitrile butadiene styrene (ABS) that contained the target compounds at 15% w/w and that were prepared and validated for the European ENFIRO project (Life Cycle Assessment of Environment-Compatible

Flame Retardants: Prototypical Case Study). Aliquots of 100 mg of polymer were extracted in triplicate with 20 ml of dichloromethane by shaking for 24 h and then an ultrasonic extraction for 10 min. The solution was diluted 200 times with toluene followed by 25 times with methanol before analysis. Percentage recoveries were 102±4 for PBDPP and 88±5 for BPA-BDPP.

The main analytical characteristic of the method are given in Table 3. The instrumental detection (LODs) and quantification limits (LOQs) were calculated from blank determinations by using a signal-to-noise ratio of 3 and 10, respectively. The quantification and detection limits of the method were estimated from these values by considering a sample amount of 50 mg, 20 mL extraction solvent and a dilution factor of 1:10 (v/v) in methanol. The whole dichloromethane extracts could be evaporated without losses of the target compounds and reconstituted in methanol to improve the detection limits if required. Instrumental quantitation limits by LC-APCI-HRTOFMS were 2.5 for PBDPP and 5 ng mL^{-1} for BPA-BDPP, that were low enough for the analysis of plastic samples (equivalent to 0.001 and 0.002 % w/w in the sample).

Possible matrix effects (ion suppression or enhancement) were assessed by spiking the final extract of three plastic samples that did not contain PBDPP and BPA-BDPP with concentrations of 0.05 and 0.2 µg mL^{-1} and were acceptable and in the ranges of 75-95% for PBDPP and of 99-120% for BPA-BDPP.

Table 3. Analytical performance of the method.

Compound	Accurate mass	Main ion in APCI+	Retention time (min)	Instrument LOD (ng mL^{-1})	Calibration		[b]Method LOQ (% w/w)	[b]Method LOD (% w/w)
					[a]Linear regression equation	R^2		
PBDPP	575.1019	[M+H]$^+$	10.9	1	y = 873903x - 330	0.9982	0.001	0.0004
BPA-BDPP	693.1802	[M+H]$^+$	14.5	2	y = 360656x - 35	0.9953	0.002	0.0008

[a]n=7, units µg mL^{-1},[b]calculated on the basis of 50 mg sample, 20 mL dichloromethane extract and 1:10 (v/v) dilution factor

Sample analysis

Concentrations of PBDPP and BPA-BDPP in consumer products are given in Table 4. The presence of PBDPP and BPA-BDPP was confirmed by retention time, mass accuracy (< 5ppm) and mSigma or isotopic pattern fitting values (below 100).

Both compounds were detected together in 7 of the 12 newly purchased products with concentrations in the ranges of 0.002-0.3 % w/w for PBDPP and 0.02-0.18 % w/w for BPA-BDPP. The higher concentrations were found in a plastic electrical adorn (0.3 % w/w PBDPP and 0.2 % w/w of BPA-BDPP) and in an electrical double adaptor (0.3 % w/w PBDPP and 0.05 % w/w of BPA-BDPP). It is worth mentioning that in 4 of the 7 samples the concentration of BPA-BDPP was between 2-10 times higher than that of PBDPP. On the other hand, 4 of the 13 samples purchased before 2006 contained PBDPP and none contained BDA-BDPP. Concentrations of 5.7 and 7.8 % w/w PBDPP were found in an old television and a printer. These high concentrations suggests that PBDPP was the main (or one of the main) flame retardants used in these two products.

Table 4. Concentration (percentage in weight material w/w) of PBDPP and BPA-BDPP in different plastic products.

|		Purchase year	PBDPP (w/w)	BPA-BDPP (w/w)	Other PFRs
Electrical powerboard	1	2012	0.002	0.01	TPHP
	2	2012	n.d.	n.d.	-
Electrical adaptor	1	2012	0.3	0.06	TPHP
	2	2012	0.02	0.05	TPHP
Plastic children toys	1	2012	n.d.	n.d.	TBOEP
	2	2012	n.d.	n.d.	-
	3	2012	0.003	0.005	-
Vacuum cleaner		2012	n.d.	n.d.	-
Electrical plastic adorn		2012	0.3	0.2	TPHP, TMPP
Heat sealer		2012	0.05	0.15	TPHP, TMPP
Television	1	2012	n.d.	n.d.	-
	2	2012	0.06	0.07	TPHP, TCEP,TMPP
	3	2002	5.7	n.d.	TPHP
	4	2006	n.d.	n.d.	-
	5	2002	n.d.	n.d.	-
	6	2005	n.d.	n.d.	-
	7	2000	0.007	n.d.	TPHP
	8	2006	n.d.	n.d.	TPHP
Old PC monitor		2000	n.d.	n.d.	-
Scanner	1	2004	n.d.	n.d.	-
	2	1998	n.d.	n.d.	-
	3	2002	n.d.	n.d.	-
Printer	1	2000	7.8	n.d.	TPHP
	2	2000	0.005	n.d.	-
	3	1998	n.d.	n.d.	-
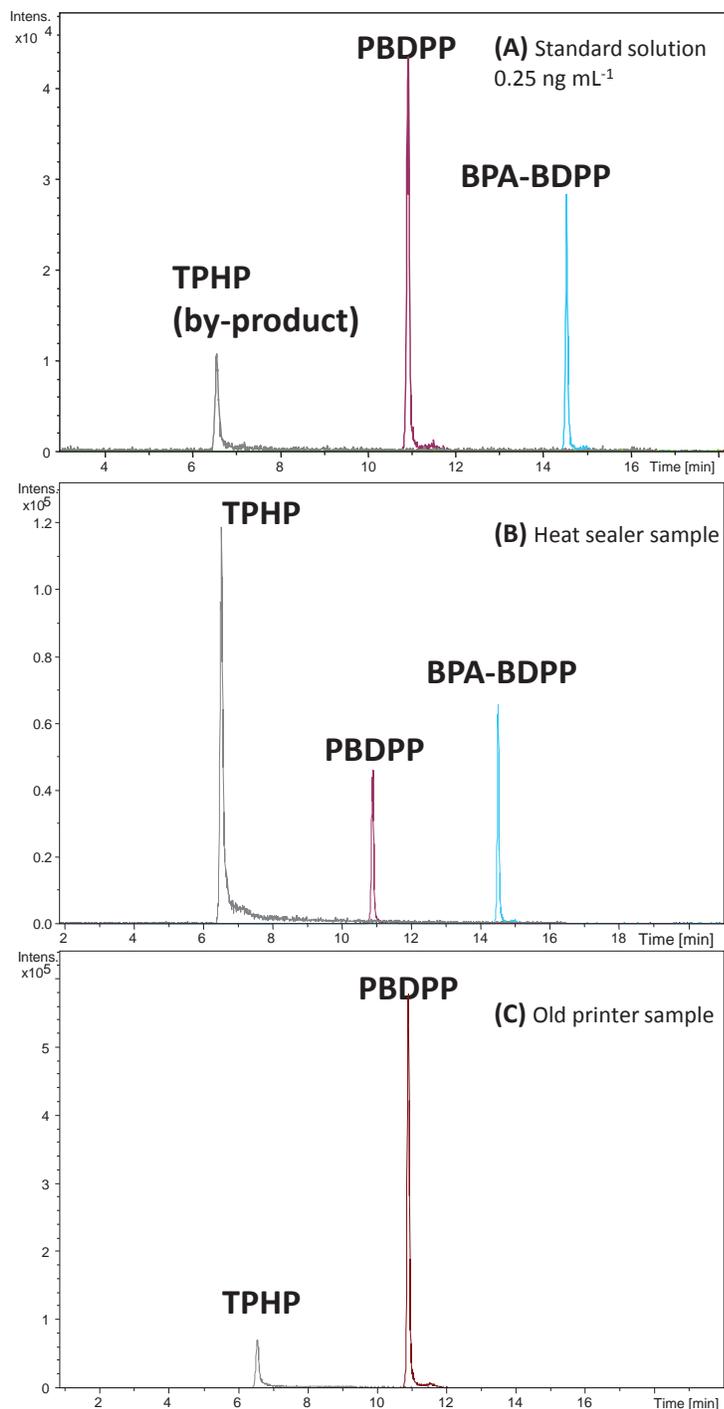
Figure 1. LC-APCI(+)-HRTOFMS extracted ion chromatograms of target compounds in (A) standard solution of PBDPP and BPA-BDPP in methanol (individual concentrations 0.25 μg mL^{-1}), a diluted heat sealer sample extract and a diluted old printer sample extract.

Although we analyzed only a limited number of samples and we can't provide any statistically significant conclusion about the changes in the use of PFRs, these results suggest that the use of BPA-BDPP has increased after the phase out of PBDEs in 2005, with PBDPP being also more frequently detected in newer products but at lower concentrations. Although the concentrations found for BPA-

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BDPP and PBDPP in the samples purchased in 2012 were not high enough to provide flame retardancy, the fact that almost half of the samples contained these compounds suggests that they may be extensively used in common household appliances and other plastic products. Their origin is not clear and they could be components of flame retardant mixtures or they could come from cross-contamination during the industrial processing or from recycled polymers. TPHP, accurate mass value 327.0781 is a by-product in the PBDPP and BPA-BDPP technical products (up to 5%) and was present in every sample containing these compounds. Figure 1 shows the extracted ion chromatograms of PBDPP, BPA-BDPP and TPHP in a standard solution and in two plastic products. In some samples, TPHP was present at a higher level than would be expected for by-product [e.g. Figure 1 (B)], so probably acting in these samples as flame retardant or plasticizer.

The presence of other PFRs was investigated and confirmed by mass accuracy (< 5ppm) and mSigma values (below 100). Besides TPHP, other PFRs were present in samples purchased in 2012. TMPP was present in two LCD televisions and the heat sealer sample. TCEP was found in one LCD television and TBOEP in one toy sample, all of them at concentrations below 0.1 % w/w. Only TPHP was detected in old plastic products (namely in four samples, in three of them probably as by-product of PBDPP).
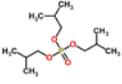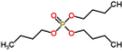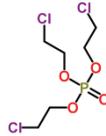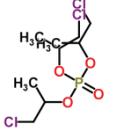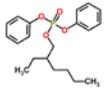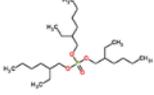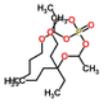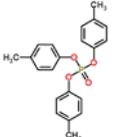

Conclusions

The method proposed for the analysis of PBDPP and BPA-BDPP in plastic products by LC-APCI-HRTOF-MS is simple and provides good recoveries (above 90%). It is a good instrumental alternative to LC-ESI-MS in terms of sensitivity and matrix effects and to common GC-MS in which broad peaks and thermal degradation usually hamper the detection of both compounds. PBDPP and BPA-BDPP have been quantified in electronic and other plastic consumer products. Until now, such data was very limited or non-existing. Both PBDPP and BPA-BDPP were detected together in 7 of the 12 products purchased in 2012 while only PBDPP was found in 4 of the 13 products purchased before 2006. Due to the low concentrations found in recent product (below 0.3 % w/w) their application or origin is not clear, being recycling one possible source. These findings call for further research on the presence and potential toxic effects of PBDPP and BPA-BDPP that may be widespread in household appliances. They further underpin recent data of our research group showing high concentrations of both compounds in dust collected on electronic equipment.

Acknowledgments

Appendix. Supplementary material

Table S1. Other organophosphorus flame retardants included in this study (name, structure, molecular formula), main ion and accurate mass value.

Target Compound		Structure	Molecular Formula	Main Ion	
				Ion	[a]Accurate
TIBP	Tris(isobutyl) phosphate		$C_{12}H_{27}O_4P$	$[M+H]^+$	267.1719
TNBP	Tris(butyl) phosphate		$C_{12}H_{27}O_4P$	$[M+H]^+$	267.1719
TCEP	Tris(2-chloroethyl) phosphate		$C_6H_{12}Cl_3O_4P$	$[M+H]^+$	284.9612
TCIPP	Tris(1-chloro-2-propanyl) phosphate		$C_9H_{18}Cl_3O_4P$	$[M+H]^+$	327.0081
DOPO	3,4:5,6-Dibenzo-2H-1,2-oxaphosphorin-2-oxide		$C_{12}H_9O_2P$	$[M+H]^+$	217.0413
TPHP	tris(phenyl) phosphate		$C_{18}H_{15}O_4P$	$[M+H]^+$	327.0781
EHDP	2-Ethylhexyl diphenyl phosphate		$C_{20}H_{27}O_4P$	$[M-C_8H_{17}+H_2]$	251.0468
TEHP	2-Ethylhexyl phosphate		$C_{24}H_{51}O_4P$	$[M+H]^+$	435.3598
TBOEP	Tris(2-butoxyethyl) phosphate		$C_{18}H_{39}O_7P$	$[M+H]^+$	399.2506
TMPP	Tris(methylphenyl) phosphate		$C_{21}H_{21}O_4P$	$[M+H]^+$	369.1250

[a]Accurate mass values calculated with Compass Isotope pattern from Data analysis 4.0 (Brukers Daltonic); [b]Compounds identified by untargeted screening

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