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

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21 **Abstract**

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

39

40 **KEYWORDS:** organophosphorus flame retardants; resorcinol bis-(diphenylphosphate);  
41 bisphenol A bis (diphenylphosphate); liquid chromatography; atmospheric pressure chemical  
42 ionization

43 **1. Introduction**

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

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

56 One such alternative class of flame retardants are the organophosphorus flame retardants (PFRs).  
57 Stapleton et al. (2012) identified tris(1,3-dichloro-2-propyl) phosphate (TDCPP) and components  
58 associated with Firemaster550, a mixture containing 2-ethylhexyl-2,3,4,5-tetrabromobenzoate  
59 (EH-TBB), bis (2-ethylhexyl) 2,3,4,5- tetrabromophthalate (BEH-TEBP) and triphenyl  
60 phosphate (TPHP), as major flame retardants in polyurethane foam from couches purchased after  
61 the phase-out of pentaBDE in 2005. Two chlorinated PFRs not previously reported in the  
62 environment, V6 and a derivative that contains tris(2-chloroethyl) phosphate (TCEP) as an  
63 impurity, were identified in baby products and dust coming from polyurethane foam (Fang et al.,  
64 2012; Stapleton et al. 2013). In a recent study on dust collected in houses from California by

65 Dodson et al. (2012), the concentration of carcinogenic chlorinated organophosphorus  
66 compounds (TCEP and 2-Propanol, 1,3-dichloro, phosphate (3:1) or TDCIPP) were found up to  
67 0.01% w/w in dust, values higher than those previously reported in the USA. In the same study,  
68 tris (2,3-dibromopropyl) phosphate (TDBPP), or brominated “Tris” was also reported for the first  
69 time in house dust and concentrations of Firemaster 550 components were higher in 2011 than  
70 2006. This compound was banned in children’s sleepwear due to its carcinogenicity.

71 In contrast to these chemicals, few data are available for two other novel organophosphorus  
72 flame retardants, resorcinol bis (diphenylphosphate) (PBDPP or RDP) and bisphenol A bis  
73 (diphenylphosphate) (BPA-BDPP or BDP). PBDPP and BPA-BDPP can be used as an  
74 alternative for decabrominated dipheyl ether (decaBDE) in TV/flat screen housings and other  
75 electronic consumer products (Lowell Center for Sustainable Production, 2005) and they are  
76 applied in a variety of polymers [PBDPP is used in acrylonitrile butadiene styrene (ABS),  
77 polycarbonate (PC)/ABS, poly(p-phenylene) oxide (PPO)/ high impact polystyrene (HIPS) and  
78 BPA-BDPP in HIPS, PC, PPO and PC/ABS (Roth et al., 2012)]. There are few toxicity data for  
79 PBDPP and BPA-BDPP, although some aquatic toxicity studies in the literature show varying  
80 results with moderate-low and high-low toxicity, respectively (Waaaijers et al., 2013). This  
81 variation may be due to the presence of triphenyl phosphate (TPHP) as a by-product in the  
82 PBDPP and BPA-BDPP technical products (up to 5%); TPHP is known to be toxic to aquatic  
83 organisms (EC10 = 0.037 mg/L for *Oncorhynchus mykiss*) (Waaaijers et al., 2013). Levels of  
84 PBDPP and BPA-BDPP have been recently reported by our research group in dust samples from  
85 the Netherlands, Greece and Sweden. High concentrations were found in dust collected on  
86 electronic equipment (<0.1-1280 µg/g for BPA-BDPP and <0.04-520 µg/g for PBDPP), while  
87 lowerlevels were measured further away from the electronics (Brandsma et al., 2013)

88 To the best of our knowledge the only data on PBDPP and BPA-BDPP are from Roth et al.  
89 (2012), who reported a method based on ultrasonic supported extraction and precipitation for the  
90 analysis of PFRs in polymer parts of electrical and electronic devices by gas chromatography-  
91 quadrupole mass spectrometry (GC-q-MS) analysis. PBDPP was found at 21.4-17.4% w/w in  
92 PPO/HIPs polymers and at 0.18 % w/w in PC polymer. BPA-BDPP was found at 3.3- 7.0% w/w  
93 in PC and at 13.2% w/w in ABS/PC polymer in samples obtained from actual and second-hand  
94 equipment as well as waste devices gathered from collection stations and recycling plants (Roth  
95 et al., 2012). In the current study we present a sensitive and selective liquid extraction followed  
96 by LC-APCI(+)-HRTOF-MS method for the quantification of PBDPP and BPA-BDPP in a  
97 variety of plastic products commonly found in the indoor environment, making them a potential  
98 route via which human exposure can occur.

## 99 **2. Material and methods**

### 100 **2.1. Chemicals and reagents**

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

107 The internal MS calibration was made with an APCI-TOF tuning mix provided by Supelco  
108 (Bellefonte, PA, USA). MS internal calibration in each run was performed by infusing the  
109 calibration solution into the source within the first minute of the chromatogram by using a

110 syringe pump (as designed by the supplier of the instrument). The internal calibration was  
111 performed by enhanced quadratic mode, being values below 5 ppm mass error considered  
112 acceptable.

## 113 **2.2. Apparatus**

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

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

## 125 **2.3. Sample extraction and analysis**

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

130 Small pieces of the samples (~50 mg, obtained with a small cutter) were extracted with 20 mL  
131 of dichloromethane (shaking for 24h and sonication for 10 min) and then 10-100 times diluted  
132 with methanol as required. Extracts were ultracentrifuged in Eppendorf microtubes (10.000  
133 rpm, 5 min) for the precipitation of minor remaining solids and aliquots of 2.5  $\mu\text{L}$  were finally  
134 injected in the LC system. The LC mobile phase consisted of water (A) and methanol (B) both  
135 containing 0.25% v/v formic acid at a flow rate of 0.3  $\text{mL min}^{-1}$ . The gradient was as follows:  
136 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  
137 removal of highly hydrophobic compounds) and finally re-conditioning for 8 min.

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

### 140 **3. Results and discussion**

#### 141 **3.1. LC-HR-TOF-MS parameters optimization**

142  
143 PBDPP and BPA-BDPP could be analyzed by both ESI and APCI sources operating in positive  
144 mode, with  $[\text{M}+\text{H}]$  as the major ion. It is well-known that the APCI source is more suitable for  
145 the analysis of non-polar compounds than the ESI source and the sensitivity was indeed around  
146 1.5 and 1.7 times higher in the APCI mode for PBDPP and BPA-BDPP, respectively.

147 MS-TOF parameters (mainly capillary exit and skimmer1: hexapole RF; transfer time and puls  
148 storage time) are dependent on the  $m/z$  value and influence sensitivity. These parameters were  
149 optimized for the  $m/z$  of interest in the range 550-700  $m/z$  (see Table 2). Although it was not the  
150 focus of this study, the presence of other PFRs in the samples was investigated for discussion of  
151 the results. A number of other PFRs and plasticizers, namely tris(butyl) phosphate (TNBP);

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

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

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



### 175 3.2. Analytical performance of the method.

176 The extraction method was validated by analyzing two polymer materials made of acrylonitrile  
177 butadiene styrene terpolymer (ABS) that contained the target compounds at 15% w/w and that  
178 were prepared and validated for the European ENFIRO project (Life Cycle Assessment of  
179 Environment-Compatible Flame Retardants: Prototypical Case Study). Aliquots of 100 mg of  
180 polymer were extracted in triplicate with 20 ml of dichloromethane by shaking for 24 h and then  
181 an ultrasonic extraction for 10 min. The solution was diluted 200 times with toluene followed by  
182 25 times with methanol before analysis. Percentage recoveries were 102±4 for PBDP and 88±5  
183 for BPA-BDPP.

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

193 Possible matrix effects (ion suppression or enhancement) were assessed by spiking the final  
194 extract of three plastic samples that did not contain PBDPP and BPA-BDPP with concentrations  
195 of 0.05 and 0.2 µg mL<sup>-1</sup> and were acceptable and in the ranges of 75-95% for PBDPP and of 99-  
196 120% for BPA-BDPP.

197

### 198 3.3. Sample analysis

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

202 Both compounds were detected together in 7 of the 12 newly purchased products with  
203 concentrations in the ranges of 0.002-0.3 % w/w for PBDPP and 0.02-0.18 % w/w for BPA-  
204 BDPP. The higher concentrations were found in a plastic electrical adorn (0.3 % w/w PBDPP  
205 and 0.2 % w/w of BPA-BDPP) and in an electrical double adaptor (0.3 % w/w PBDPP and 0.05  
206 % w/w of BPA-BDPP). It is worth mentioning that in 4 of the 7 samples the concentration of  
207 BPA-BDPP was between 2-10 times higher than that of PBDPP. On the other hand, 4 of the 13  
208 samples purchased before 2006 contained PBDPP and none contained BDA-BDPP.  
209 Concentrations of 5.7 and 7.8 % w/w PBDPP were found in an old television and a printer.  
210 These high concentrations suggests that PBDPP was the main (or one of the main) flame  
211 retardants used in these two products.

212 Although we analyzed only a limited number of samples and we can't provide any statistically  
213 significant conclusion about the changes in the use of PFRs, these results suggest that the use of  
214 BPA-BDPP has increased after the phase out of PBDEs in 2005, with PBDPP being also more  
215 frequently detected in newer products but at lower concentrations. Although the concentrations  
216 found for BPA-BDPP and PBDPP in the samples purchased in 2012 were not high enough to  
217 provide flame retardancy, the fact that almost half of the samples contained these compounds  
218 suggests that they may be extensively used in common household appliances and other plastic

219 products. Their origin is not clear and they could be components of flame retardant mixtures or  
220 they could come from cross-contamination during the industrial processing or from recycled  
221 polymers. Triphenyl phosphate (TPHP, accurate mass value 327.0781) is a by-product in the  
222 PBDPP and BPA-BDPP technical products (up to 5%) and was present in every sample  
223 containing these compounds. Figure 1 shows the extracted ion chromatograms of PBDPP, BPA-  
224 BDPP and TPHP in a standard solution and in two plastic products. In some samples, TPHP was  
225 present at a higher level than would be expected for by-product [e.g. Figure 1 (B)], so probably  
226 acting in these samples as flame retardant or plasticizer.

227 The presence of other PFRs was investigated and confirmed by mass accuracy ( $< 5\text{ppm}$ ) and  
228 mSigma values (below 100). Besides TPHP, other PFRs were present in samples purchased in  
229 2012. TMPP was present in two LCD televisions and the heat sealer sample. TCEP was found in  
230 one LCD television and TBOEP in one toy sample, all of them at concentrations below 0.1 %  
231 w/w. Only TPHP was detected in old plastic products (namely in four samples, in three of them  
232 probably as by-product of PBDPP).

#### 233 **4. Conclusions**

234 The method proposed for the analysis of PBDPP and BPA-BDPP in plastic products by LC-  
235 APCI-HRTOF-MS is simple and provides good recoveries (above 90%). It is a good  
236 instrumental alternative to LC-ESI-MS in terms of sensitivity and matrix effects and to common  
237 GC-MS in which broad peaks and thermal degradation usually hamper the detection of both  
238 compounds. PBDPP and BPA-BDPP have been quantified in electronic and other plastic  
239 consumer products. Until now, such data was very limited or nonexistent. Both PBDPP and  
240 BPA-BDPP were detected together in 7 of the 12 products purchased in 2012 while only PBDPP

241 was found in 4 of the 13 products purchased before 2006. Due to the low concentrations found in  
242 recent product (below 0.3 % w/w) their application or origin is not clear, being recycling one  
243 possible source. These findings call for further research on the presence and potential toxic  
244 effects of PBDPP and BPA-BDPP that may be widespread in household appliances. They further  
245 underpin recent data of our research group showing high concentrations of both compounds in  
246 dust collected on electronic equipment.

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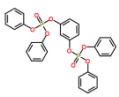
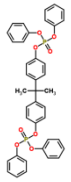
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319

**Table 1**[Click here to download Table: Table 1.docx](#)**Table 1. Physico-chemical information of PBDPP and BPA-BDPP**

Abbreviation	CAS number	Chemical name	Structure	Formula	<sup>a</sup> LogKow	<sup>a</sup> Vapour pressure (Pa)
PBDPP	57583-54-7	Resorcinol bis(biphenylphosphate)		C <sub>30</sub> H <sub>24</sub> O <sub>8</sub> P <sub>2</sub>	7.08	5.01E-11
BPA-BDPP	5945-33-5	Bisphenol A bis(bisphenylphosphate)		C <sub>39</sub> H <sub>34</sub> O <sub>8</sub> P <sub>2</sub>	8.29	1.97E-15

<sup>a</sup>values reported by Bergman et al., 2012



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

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<b>APCI source</b>	<b>HR-TOFMS</b>
Capillary -1000 V	Capillary exit: $\pm 100$ V
End plate offset -500	Skimmer1: $\pm 33$ V
Corona +5000 nA	Hexapole 1: 23 V
Dry gas 2 L min <sup>-1</sup>	Hexapole RF: 200 V
Nebulizer 2 bar	Transfer time: 70
Dry Heater 220 °C	Puls storage time: 15
Vaporizer temperature at 240 °C	

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**Table 3**[Click here to download Table: Table 3.docx](#)**Table 3. Analytical performance of the method**

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

<sup>a</sup>n=7, units µg mL<sup>-1</sup>; <sup>b</sup>calculated on the basis of 50 mg sample, 20 mL dichloromethane extract and 1:10 (v/v) dilution factor

**Table 4**[Click here to download Table: Table 4.docx](#)**Table 4. Concentrations (percentage in weight material w/w) of BPA-BDPP and PBDPP 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 captions**

**Figure 1.** LC-APCI(+)-HRTOFMS extracted ion chromatograms of target compounds in (A) standard solution of PBDPP and BPA-BDPP in methanol (individual concentrations  $0.25 \mu\text{g mL}^{-1}$ ), a diluted heat sealer sample extract and a diluted old printer sample extract

Figure 1

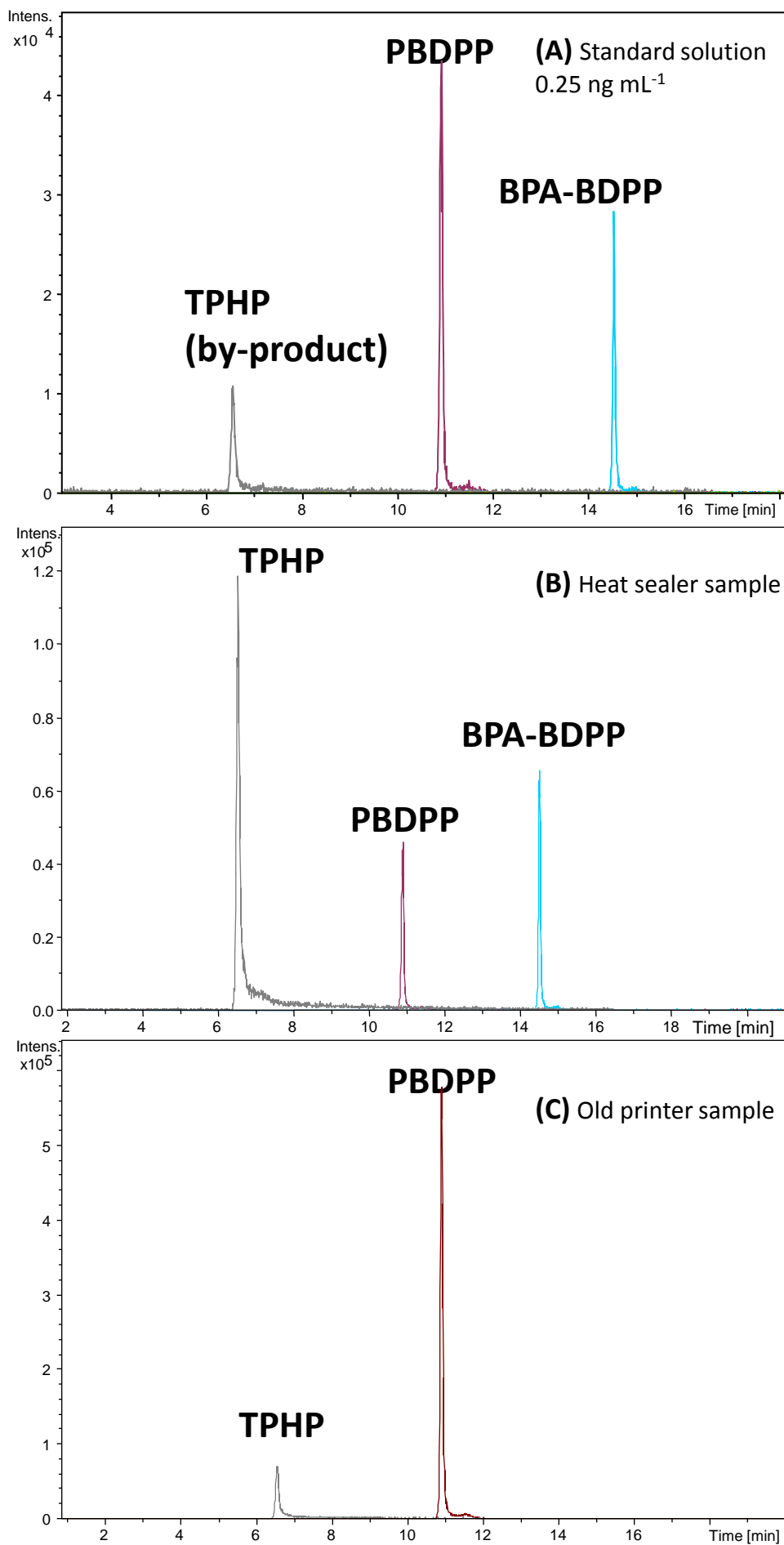


Figure 1