

14 **Abstract**

15 A sensitive method for the simultaneous quantification of dechloranes, polybrominated diphenyl
16 ethers (PBDEs), and novel brominated flame retardants (NBFRs) has been developed for gas
17 chromatography (GC) coupled to tandem mass spectrometry operating in electron capture negative
18 ionization (ECNI) mode. The major advance has been achieved by combining selected ion monitoring
19 (SIM) and multiple reaction monitoring (MRM) modes in well-defined time windows, to determine
20 dechloranes, PBDEs and NBFRs at pg g^{-1} level in one single analysis in complex matrix biological
21 samples. From the chromatographic point of view, efforts were devoted to study several injection
22 modes using multimode inlet (MMI) in order to obtain low instrumental detection limits, necessary for
23 trace compounds such as Dechlorane Plus (DP) isomers. Method performance was also evaluated:
24 calibration curves were linear from $20 \text{ fg } \mu\text{L}^{-1}$ to $100 \text{ pg } \mu\text{L}^{-1}$ for the studied compounds, with method
25 detection limits at levels of 50 fg g^{-1} for DPs. Repeatability and reproducibility, expressed as relative
26 standard deviation, were better than 5% even in solvent vent mode for the injection of standards. The
27 application to a wide range of complex samples (including food, human, and animal serum samples)
28 indicated a sensitive and reliable way to quantify at the pg g^{-1} level four HNs, Dechlorane Plus (*anti*-DP
29 and *syn*-DP) and two of their homologues (Dechlorane-602 and Dechlorane-603), 11 PBDE congeners
30 (no. 28, 47, 49, 66, 85, 99, 100, 153, 154, 183, and 209), and five novel BFRs, *i.e.*, decabromodiphenyl
31 ethane (DBDPE), 1,2-bis(2,4,6-tribromo-phenoxy)ethane (BTBPE), hexabromobenzene (HBB), 2,3,4,5-
32 tetrabromo-ethylhexyl-benzoate (TBB) and tetrabromophthalate (TBPH).

33

34 **Keywords**

35 Chemical ionization, gas chromatography, brominated flame retardants, Dechloranes, large volume
36 injection, biological matrices

37

38 1. Introduction

39 Halogenated flame retardants (HFRs), including chlorinated and brominated compounds, are used to
40 prevent ignition and combustion of flammable materials, widely employed in furniture, plastics, foams,
41 and textile upholstery, among other products [1]. HFRs have been detected in various environmental
42 and food samples as they are released into air, soil and water due to manufacture, improper handling,
43 and disposal of HFR-containing products and materials [2]. Among them, polybrominated diphenyl
44 ethers (PBDEs) have been extensively investigated, as a consequence of their past usage, toxicity and
45 persistence in the food chain [3, 4]. As a result of bans applied to commercial PBDE mixtures, there is
46 an increasing production and use of alternative HFRs [5, 6]. Nevertheless, apart from monitoring these
47 HFRs, the determination of PBDEs is still necessary for monitoring purposes and to assess their
48 replacement efficiency [7, 8]. A scheme displaying the different structures of the investigated HFRs is
49 shown in **Figure 1**.

50 There is a large amount of literature regarding the analysis of PBDEs and novel brominated flame
51 retardants (NBFRs) by gas chromatography–mass spectrometry (GC-MS) and GC-MS/MS using electron
52 capture negative ionization (ECNI) and electron ionization (EI) [9]. More recently, atmospheric
53 pressure chemical ionization (APCI) [10, 11] has also been reported for the analysis of brominated FRs.
54 Both ECNI and APCI offer good sensitivity when compared to EI, while the specificity when using APCI
55 and EI in MS/MS experiments is higher than the obtained by monitoring bromide ions in ECNI [10]. For
56 the determination of Dechloranes, the majority of studies performed so far used EI-MS(/MS), with
57 insufficient detection limits in some cases [12, 13] or ECNI-MS(/MS) with the need of an additional
58 injection, separated from PBDEs [14–16]. GC-EI-MS/MS methods monitor transitions derived from the
59 molecular ion to m/z 237 and m/z 228 [16]. Similar to PBDEs, the analysis of DPs can benefit of selecting
60 more specific transitions coming from the molecular ion by using softer ionization sources. DP isomers
61 constitute a special case study, as they have quite a particular fragmentation behaviour. Several
62 studies have investigated the different fragmentation of *anti*- and *syn*- DP isomers under variable ECNI

63 source temperatures, either in full-scan [17] or in SIM experiments [15], but not yet in MRM
64 experiments.

65 Human biomonitoring data on dechloranes is not extensive, but there are few articles on studies
66 investigating their presence and levels in serum, e.g. from China, where the highest levels have been
67 reported near e-waste recycling plants [18–20], and from Canada [21], Norway [22, 23] or Germany
68 [24]. In all these studies, the limits of detection for DPs were in the pg g^{-1} level.

69 Against this background, the availability of a method with the benefits of sensitivity and specificity for
70 Dechloranes and sensitivity for PBDEs and other flame retardants in a single analysis using a chemical
71 ionization (CI) source in negative mode could be beneficial for monitoring laboratories. The aim of this
72 work was the development of a methodology for the simultaneous analysis of HFRs of high concern at
73 low pg g^{-1} levels in a wide range of complex samples, such as food, human and animal serum samples.
74 Such improvement of the analytical methods will be useful in the currently running biomonitoring
75 schemes, such as the Flemish Environment and Health study.

76

77 **2. Materials and methods**

78 **2.1. Chemicals and reagents**

79 Standards of BDE-28, -49, -47, -99, -100, -153, -154, -138, -183, and -209, 1,2-Bis(2,4,6-
80 tribromophenoxy)ethane (BTBPE), *syn*-DP and *anti*-DP isomers, 2-ethylhexyl-2,3,4,5 tetrabromo-
81 benzoate (TBB), 2,3,4,5-tetrabromophthalate (TBPH), hexabromobenzene (HBB), dechlorane-602
82 (Dec-602), dechlorane-603 (Dec-603), isotopically labelled internal standards (IS) ^{13}C -BDE-209, ^{13}C -
83 TBPH, ^{13}C -TBB, ^{13}C -*syn*-DP, and ^{13}C -*anti*-DP were purchased from Wellington Laboratories (Guelph, ON,
84 Canada). Recovery standard (RS) CB-207 was purchased from Dr. Ehrenstorfer Laboratories (Augsburg,
85 Germany). Polypropylene (PP) tubes (15 mL) were obtained from Greiner Bio-one (Belgium). Empty PP
86 cartridges (25 mL) were purchased from Grace (Lokeren, Belgium), while Florisil® cartridges (500 mg,
87 3 mL) and empty PP cartridges (6 mL) were purchased from Supelco (Bellefonte, PA, USA). Silica gel,
88 anhydrous sodium sulphate (Na_2SO_4) and concentrated sulfuric acid (H_2SO_4 , 98%) were purchased from

89 Merck (Darmstadt, Germany). All solvents were of chromatography grade: n-hexane was purchased
90 from Acros Organics (Belgium); dichloromethane (DCM), iso-octane, toluene and acetonitrile (ACN)
91 were purchased from Merck.

92

93 **2.2 Sample Treatment**

94 Food samples (including biscuits, smoked salmon, and chicken eggs) were treated as indicated in a
95 previous work [25]. Briefly, samples were homogenized, freeze-dried, and stored at -20 °C until
96 analysis. The samples were weighted in pre-washed 15 mL polypropylene (PP) tubes, and spiked with
97 the IS mixture. After spiking, samples were extracted by solid-liquid extraction (SLE) with ACN:toluene
98 (9:1, v/v) . After a two-step clean-up (performed on Florisil® and acidified silica 5%), the samples were
99 evaporated to dryness and reconstituted in 100 µL of the recovery standard (RS) (CB-207 in iso-
100 octane:toluene; 9:1, v/v) and transferred to amber injection vials for GC-ECNI-MS(/MS) analysis.

101 Serum samples including hyena, cheetah and lion (Zoo Antwerp, Belgium), sea eagle plasma
102 (Trondheim, Norway) and human cord blood (Flemish Environment and Health study II – Flemish
103 newborns) were extracted according to the method described elsewhere [26], with slight
104 modifications. Solid-phase extraction (SPE) on OASIS HLB cartridges was used followed by clean-up on
105 1 g of acidified silica 44% and eluted with 10 mL n-hexane:dichloromethane (1:1, v/v). The cleaned
106 extract was evaporated to incipient dryness and re-dissolved in 100 µL iso-octane.

107

108 **2.3 GC-(ECNI)-MS(/MS)**

109 The chromatographic analysis was performed using an Agilent 7890B gas chromatograph, equipped
110 with an Agilent 7693A autosampler with Multimode Inlet (MMI), coupled to a triple quadrupole mass
111 spectrometer, 7000C (Agilent Technologies Inc., Palo Alto, CA, USA), with a CI source working in
112 electron capture negative ionization mode. Methane was used as reagent gas at a flow of 2 mL min⁻¹.

113 The GC separation was performed using a fused silica a ZB-semivolatiles capillary column (5% phenyl-

114 arylene-95% dimethyl-polysiloxane) with a length of 20 m x 0.18 mm ID and a film thickness of 0.18
115 μm (Phenomenex, Torrance, CA, USA) working at a ramped flow from 1 mL min^{-1} (14 min) with 10 mL
116 min^{-1} to 2 mL min^{-1} (10.9 min) of helium (99.999 %; Air Liquide, Liège, Belgium). The oven program was
117 set as follows: 90 °C (1.25 min); 30 °C min^{-1} to 240 °C; then 10 °C min^{-1} to 325 °C, stay 10.4 min with a
118 total run time of 25 min. The injection of 2 μL of sample extracts was performed in cold pulsed splitless
119 mode with at a temperature of 80 °C and a pulse time of 1.25 min. The pulse pressure was set to 50.0
120 psi, with a split purge flow of 50 mL min^{-1} and purge time of 1.25 min.

121

122 3. Results and discussion

123 3.1. MS optimization

124 Optimal m/z values for SIM of each compound were selected according to [27], while the optimal MRM
125 transitions for DPs were taken from reference [28], also considering the common fragmentation
126 pattern for every compound, usually leading to bromide ions. To achieve maximum sensitivity,
127 different collision energies were tested to study the fragmentation of *syn*- and *anti*-DPs in the collision
128 cell. Two ions from the isotopic pattern corresponding to M^+ ($M+4$ and $M+6$) were selected in the first
129 quadrupole and fragmentation was performed using a range of collision energies between 5 eV and
130 35 eV. A collision energy of 5 eV was optimal for the ^{13}C -labelled DPs, while 10 eV was selected for the
131 native *syn*- and *anti*- DPs. Accordingly, the selected transitions were $654 \rightarrow 35$; $654 \rightarrow 37$ and $652 \rightarrow 35$
132 corresponding to the fragmentation of the precursor m/z ions $[M+6]^-$ and $[M+4]^-$ for the native DPs
133 and $664 \rightarrow 35$ and $664 \rightarrow 37$ taking $[M+6]^-$ m/z ion as precursor for the ^{13}C - DPs.

134 The source temperature was also optimized pursuing the maximum response for every analyte.
135 Previous studies, [17] and [15], demonstrated that low source temperatures favour the detection of
136 the molecular ion cluster, while higher temperatures (250 °C) had different effects on both isomers.
137 According to De la Torre et al [17], a temperature of 150 °C provided similar spectra for both isomers,
138 with the most abundant cluster being the one corresponding to the molecular ion $[M]^-$. However, at
139 250 °C, the two isomers showed a different pattern. In the case of *syn*-DP, the cluster corresponding

140 to the ion $[M-6Cl]^-$ became the most abundant. Summarizing, higher temperature source provided
141 more energy, hence favouring the dissociative electron capture process and increasing the abundance
142 of fragment ions, whereas lower temperatures enhanced molecular ion abundance.
143 Accordingly, after obtaining low collision energies as the optimal for the determination of DPs, we
144 theorized that low source temperatures might enhance the formation in the ion source of the parent
145 ions for the DPs transitions. Hence, source temperatures of 250 °C, 225 °C, and 200 °C were tested. An
146 increase in the response of DPs was seen at lower source temperatures (**Figure 2**), while too low
147 temperatures could affect the sensitivity for PBDEs, for which detection relies in the fragmentation to
148 the bromide ion m/z 79. The temperature of 200 °C was hence chosen as a compromise for these
149 experiments. Selected quantification and qualification transitions and ions for each analyte are
150 summarized in **Table 1**. These findings add to the previous studies on the behaviour of DPs at different
151 source temperatures, as in MRM experiments, the formation of an abundant molecular pattern to be
152 selected as a parent ion, has been proved more sensitive than a high in-source fragmentation, which
153 leads to larger losses of chlorine atoms before entering in the first quadrupole.

154

155 **3.2. Analytical parameters**

156 To maximize the signal obtained for each analyte, the use of the multimode inlet in large volume
157 injection mode was considered. The possibility of starting at a low inlet temperature allowed the
158 injection of a higher volume of extract. Therefore, several injection configurations were tested: cold
159 pulsed splitless (2 μ L), and solvent vent (5 μ L, 2 x 5 μ L and 3 x 5 μ L). **Figure 3** highlights the response
160 enhancement for the DP congeners when working at the three selected working conditions. Although
161 solvent vent injections enhance the sensitivity for DPs as well as for the rest of the selected
162 compounds, reproducibility and overloading issues were noticed when injecting extracts from fatty
163 matrices, so the injection of 2 μ L in cold pulsed splitless mode was selected as optimal. To test the
164 reliability of the method, the repeatability of absolute area was studied in five repeated injections of
165 standards at five different levels (20 $\text{fg } \mu\text{L}^{-1}$, 100 $\text{fg } \mu\text{L}^{-1}$, 1 $\text{pg } \mu\text{L}^{-1}$, 20 $\text{pg } \mu\text{L}^{-1}$ and 100 $\text{pg } \mu\text{L}^{-1}$). The relative

166 standard deviation was below 5%. Linearity of the relative response of the different compounds (to
167 their ^{13}C isotopically labelled or BDE internal standards) was studied by analyzing standard solutions,
168 in triplicate (five levels), in the range of $20\text{ fg }\mu\text{L}^{-1}$ to $100\text{ pg }\mu\text{L}^{-1}$. The correlation coefficients (r^2) were
169 higher than 0.99 for every compound, with residuals lower than 2%. Special attention has to be paid
170 to the method sensitivity for DPs, which can be derived from **Figure 2** (injection of a $16\text{ fg }\mu\text{L}^{-1}$ standard
171 solution in isooctane). Instrumental limits of detection (iLODs) were calculated as the lowest
172 concentration level giving a signal-to-noise ratio (S/N) of 3. These iLODs were determined to be around
173 $1\text{ fg }\mu\text{L}^{-1}$ for *syn*-DP and $0.5\text{ fg }\mu\text{L}^{-1}$ for *anti*-DP, when injecting $2\text{ }\mu\text{L}$ in cold pulsed splitless mode. The
174 iLODs were even lower when using solvent vent mode, as can be seen in **Figure 3**. Obtained iLODs are
175 summarized in **Table 1**. LODs and LOQs in real samples were estimated using the same criteria, by
176 extrapolation from the lowest responses (detectable and quantifiable) of every compound within the
177 analysed samples. These results are relevant especially for DP isomers, as their LODs and LOQs have
178 been lowered sensibly in comparison to previous studies. **Table 2** lists the majority of previous studies
179 performed to detect and quantify DP isomers, indicating the systems used and the achieved
180 performance in each case in terms of LOD and LOQ.

181

182 **3.3. Analysis of real samples**

183 The enhanced capabilities of the presented method were finally tested using extracts of samples of
184 food and human and animal serum previously analysed by GC-ECNI-MS, according to the method used
185 for routine analysis and described elsewhere [25]. The developed methodology allowed the
186 determination of trace quantities (below pg g^{-1} range) of the selected PBDEs in several samples. In
187 these samples, NBFs could also be evidenced. A good agreement was found when comparing the
188 quantification results of the new methodology with those given by the validated reference method
189 [25] (at the levels achievable by the reference method).

190 Special emphasis was made on the capability of the methodology to detect DPs in most of analysed
191 samples. Due to the presence of these compounds in the procedural blanks, only the samples with DPs

192 relative area higher than 10 times their corresponding relative area in the blank were quantified. The
193 most remarkable results to highlight are: a pool of four cord blood human serum samples with 0.13
194 and 0.19 pg g^{-1} of *syn*-DP and *anti*-DP, respectively; a sea eagle plasma sample with 1.95 pg g^{-1} of *syn*-
195 DP and 26 pg g^{-1} of *anti*-DP, a chicken egg with 9 ng g^{-1} of *syn*-DP and 29 ng g^{-1} of *anti*-DP and a hyena
196 serum sample with 0.33 pg g^{-1} of *syn*-DP. Dec-603 and Dec-602 were also quantified in human/animal
197 serum ranging from 5 to 66 pg g^{-1} . Chromatograms with the quantification transition of DP isomers in
198 the mentioned samples can be seen in **Figure 4 (4A)** for a procedure blank, biscuits, smoked salmon,
199 chicken egg and hyena extracts, and **4B** showing a cheetah serum, human cord blood (pool), sea eagle
200 serum, and two chicken egg extracts). **Table 3** summarizes the concentration found for each analyte
201 in the samples.

202 The most contaminated samples corresponded, as expected, to captive animals from the Antwerp Zoo
203 and the eggs of wild birds. It is also important to consider the differences found in the f-anti value.
204 *Anti*-DP has been found to degrade faster than *syn*-DP at high temperatures and at e-waste sites [18],
205 so the differences measured with this methodology, for example in the hyena sample, could help to
206 assess for the degradation of these compounds in areas close to recycling facilities and monitor
207 their presence of them in animals and humans.

208

209 **4. Conclusions**

210 The use of a method combining SIM and MRM acquisition modes in an ECNI source has demonstrated
211 high sensitivity for a wide range of HFRs, specifically for DP isomers, which have been detected in most
212 of analyzed samples, including procedural blanks. This combination of acquisition modes together with
213 large volume injections allowed decreasing the LODs for DPs to fg g^{-1} levels, which constitutes a
214 significant advancement compared to previous methodologies monitoring the molecular ion in SIM
215 mode or less sensitive transitions in EI-MS/MS. Nevertheless, the use of large volume injections can
216 be an issue for some fatty matrices and has to be carefully applied to selected samples. The method
217 was applied to a wide range of complex matrices and was able to quantify DP isomers at low pg g^{-1}

218 levels in serum samples. This methodology is an important tool for the determination of HFRs at ultra-
219 trace levels in food and biological samples, helping to monitor the release and occurrence of PBDEs,
220 HNs and NBFRs in the environment.

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222

223 **Acknowledgments**

224 The authors acknowledge the financial support of Universitat Jaume I (UJI-A2016-01) and Generalitat
225 Valenciana, (research group of excellence PROMETEO/2009/054 and PROMETEO II 2014/023 and
226 Collaborative Research on Environment and Food-Safety (ISIC/2012/016)). Carlos Sales acknowledges
227 the COST Action ES1307 for the STSM grant which made possible his stay at the Toxicological Centre
228 of Antwerp. Dr. Giulia Poma and Dr. Govindan Malarvannan acknowledge the University of Antwerp
229 for their postdoctoral fellowships.

230

231 **Conflict of interest**

232 The authors declare that they have no conflict of interest.

233

234 **Figure Captions**

235 **Fig. 1** Scheme of the structures of the main compounds selected for the study.

236 **Fig. 2** Variation in the peak area for the most sensitive MRM transition for DPs, for the injection of a
237 standard mixture at $16 \text{ fg } \mu\text{L}^{-1}$ in isooctane at different source temperatures (200 °C, 225 °C and 250
238 °C).

239 **Fig. 3** Graphical comparison of the methodology performance for the injection of a DP mixture (16 fg
240 μL^{-1}). S/N = signal to noise ratio.

241 **Fig. 4** Chromatograms corresponding to the quantification transition of DPs for the injection of (A)
242 procedural blank, biscuits, smoked salmon, chicken egg and hyena serum extracts, and (B) cheetah
243 serum, human cord blood serum, chicken egg and sea eagle serum extracts.

244

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329 norbornene flame retardants in environmental and biota matrices by gas chromatography
330 coupled to tandem mass spectrometry. *J Chromatogr A* 1248:154–160.
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332

333 **Table 1.** Analytical performance of the method including MS quantitation parameters.

Compounds	RT	Q	q	iLOD (fg μL^{-1})		
				2 μL	5 $\mu\text{L SV}$	10 $\mu\text{L SV}$
BDE 28	8.05	79	81	20	10	5
BDE 49	9.06	79	81	20	10	5
BDE 47	9.26	79	81	10	5	2.5
BDE 66	9.51	79	81	20	10	5
BDE 100	10.36	79	81	20	10	5
BDE 99	10.72	79	81	20	10	5
BDEs 85	11.40	79	81	20	10	5
BDE 154	11.69	79	81	20	10	5
BDE 153	12.24	79	81	20	10	5
BDE 138	12.95	79	81	20	10	5
BDE 183	13.74	79	81	20	10	5
BDE 209	21.04	487	489	200	100	50
HBB	8.80	79	81	20	10	5
TBB	10.65	357	359	200	100	50
DEC602	10.70	612	35	250	120	60
DEC603	13.30	638	35	100	50	25
BTBPE	14.18	79	81	20	10	5
TBPH	14.60	384	515	100	50	25
s-DP	14.90	654>35	654>37	1	0.5	0.25
a-DP	15.22	654>35	654>37	0.5	0.25	0.125
DBDPE	23.95	79	81	1000	500	250

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336**Table 2.** Techniques and conditions previously used for the determination of DP isomers and their performance in terms of LOD and LOQ

Nº	Technique	Column	Separation	m/z	LOD	LOQ	Ref
1	GC-ECNI-MS	DB-5 (15 m × 0.25 mm × 0.10 µm)	90 °C (1,5 min); 10 °C/min to 300 °C (3 min); 40 °C/min to 310 °C (5 min)	[M-H] ⁻ ; 650, 652	n.a.	2 ng g ⁻¹ (DUST)	[6]
2	GC-APCI-HRqTOFMS	DB-5 HT (15 m × 0.25 mm × 0.10 µm)	110 °C; 40 °C/min to 200 °C; 10 °C/min to 280 °C; 30 °C/min to 330 °C (5 min)	[M] ⁺ ; 653.711	0.16 pg µL ⁻¹	n.a.	[11]
3	GC-EI-HRMS	DB-5 (15 m × 0.25 mm × 0.10 µm)	120 °C (1 min); 30 °C/min to 240 °C; 5 °C/min to 275 °C; 40 °C/min to 320 °C (3 min)	[M-C ₁₃ H ₁₂ Cl ₆] ⁺ ; 271.8102; 273.8072	0.5 pg g ⁻¹ (sediment), 15 pg g ⁻¹ (fish)	n.a.	[13]
4	GC-ECNI-MS	DB-5 (30 m × 0.25 mm × 0.25 µm) DB-35 (30 m × 0.25 mm × 0.25 µm) (confirmation)	80 °C (2 min); 10 °C/min to 285 °C (5 min)	[M-H] ⁻ ; 650.652	30 pg g ⁻¹ (sediment)	n.a.	[14]
5	CZC-GC/ECNI-TOFMS	Rtx- PCB (15 m × 0.25 mm × 0.25 µm) plus Rxi-17 (1 m × 0.18 mm × 0.18 µm)	140 °C (2 min); 30 °C/min to 280 °C; 5 °C/min to 300 °C (10 min)	[M-H] ⁻ ; 650, 652	3 pg (iLOD)	n.a.	[16]
6	GC-ECNI-MS	DB-XLB (30 m × 0.25 mm × 0.25 µm)	110 °C (1 min); 8 °C/min to 180 °C (1 min); 2 °C/min to 240 °C (5 min); 2 °C/min to 280 °C (15 min); 10 °C/min to 310 °C (5 min)	[M] ⁺ ; 653.8 and 651.8	n.a.	3.08 pg g ⁻¹ fat (serum) (s-DP), 1.29 pg g ⁻¹ fat (serum) (a-DP)	[19]
7	GC-ECNI-MS	DB-1MS (30 m × 0.25 mm × 0.25 µm)	120 °C (1 min), 10 °C/min to 300 °C (8 min); 10 °C/min to 310 °C (12 min)	[M] ⁻ ; 651.7 and 653.7	40 pg g ⁻¹ l.w. (s-DP), 120 pg g ⁻¹ l.w. (a-DP), (serum)	n.a.	[21]
8	GC-ECNI-MS	DB-5 (15 m × 0.25 mm × 0.10 µm)	50 °C, 25 °C/min to 300 °C (5 min)	[M] ⁻ ; 653.8 and 651.8	1.1 pg mL ⁻¹ (serum) (s-DP), 3.3 pg mL ⁻¹ (serum) (a-DP)	3.5 pg mL ⁻¹ (serum) (s-DP), 10 pg mL ⁻¹ (serum) (a-DP)	[22]

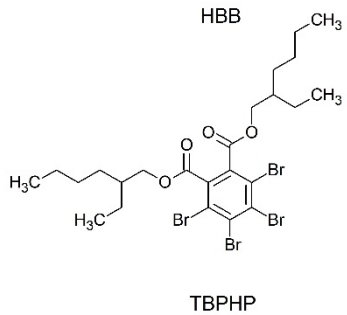
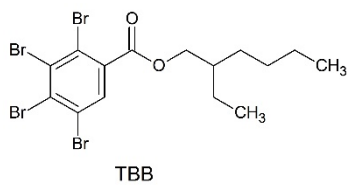
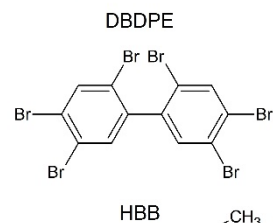
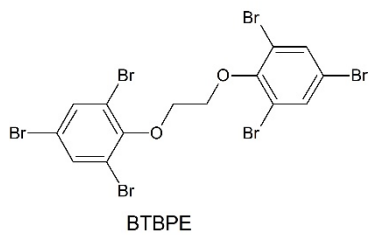
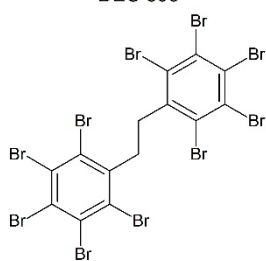
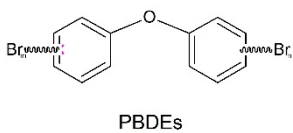
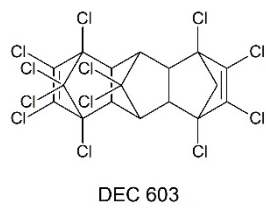
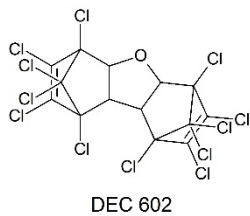
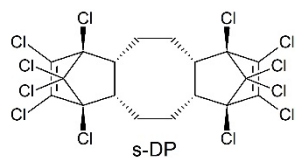
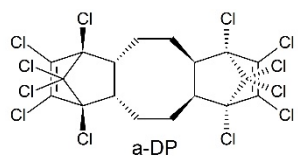
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n.a. – not available

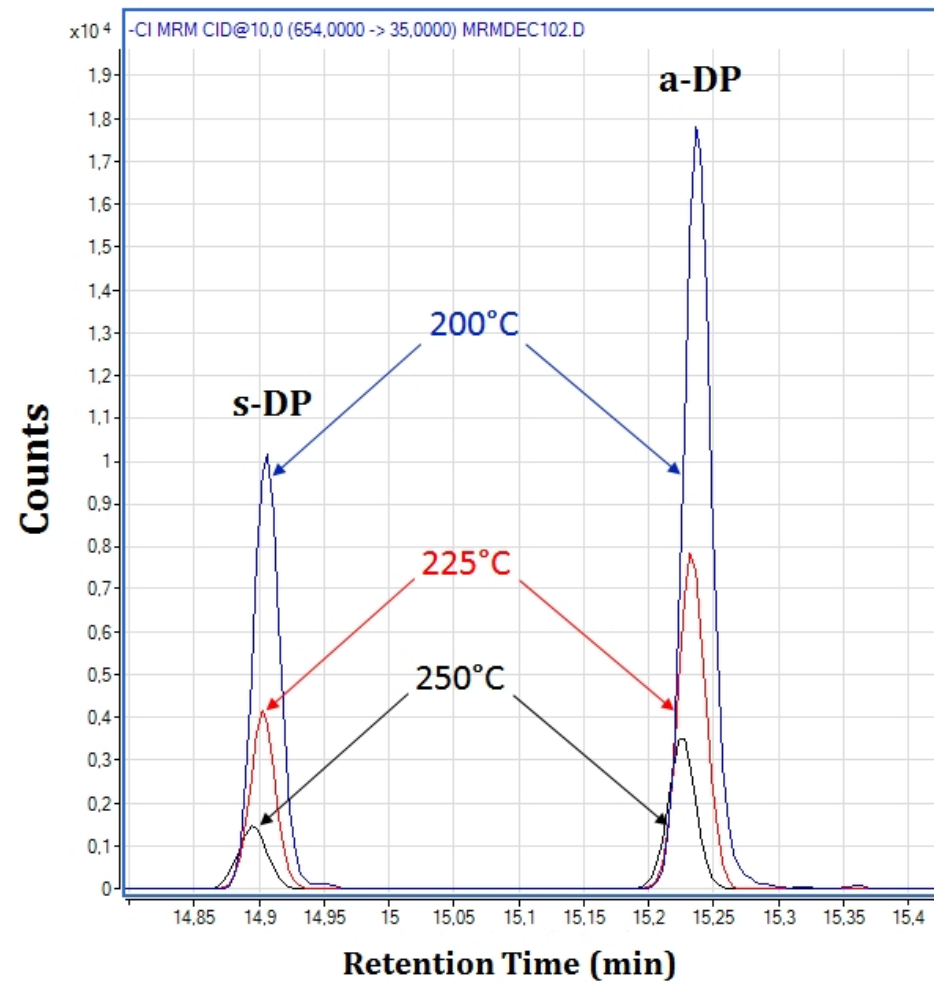
Table 3. Concentrations of PBDEs and other HFRs ($\mu\text{g g}^{-1}$) in the analyzed samples.

Compounds	LOD ($\mu\text{g g}^{-1}$)	LOQ ($\mu\text{g g}^{-1}$)	Biscuits	Smoked Salmon	Chicken Egg	Hyena Serum	Cheetah Serum	Lion serum	Human Cord Blood Pool	Blank	Chicken Egg	albumin	Chicken Egg	Sea Eagle Plasma	Sea Eagle Plasma
DEC602	1	2.5	<1	<1	<1	<1	66	12	<1	<1	5	<1	8	<1	14
DEC603	1	2.5	<1	<1	<1	8	19	8	<2.5	<1	<2.5	<1	<2.5	9	<1
syn-DP	0.03	0.10	<0.03	<0.03	<0.03	0.33	2.5	13	0.13	<0.03	9000	4	2680	1.95	<0.03
anti-DP	0.05	0.15	<0.05	<0.05	<0.05	<0.15	6	18	0.19	<0.05	29000	6	3450	22	<0.05
Σ DPs			<0.03	<0.03	<0.03	0.33	9	31	0.32	<0.003	38000	10	6128	24	<0.003
fAnti			--	--	--	--	0.71	0.58	0.59	--	0.76	0.4	0.56	0.92	
BDE 28	0.8	20	<0.8	<0.8	<0.8	<0.8	<20	<0.8	<0.8	<0.8	<0.8	<0.8	26	<0.8	<0.8
BDE 49	0.3	1	<0.3	35	<1	<0.3	<0.3	<1	<0.3	<1	220	<1	70	1	12
BDE 47	0.7	3	41	233	44	<3	11	4.5	<0.7	<0.7	540	6	455	3	16
BDE 66	1	10	<1	<1	<10	<1	<1	<1	<1	<1	<1	<10	46	<1	<1
BDE 100	0.4	4	9	51	6	<0.4	<0.4	4	<0.4	<0.4	440	7	270	4	4
BDE 99	0.5	2	18	7	5	8	8	2	<2	<0.5	1390	26	587	3	6
BDE 85	3	9	<9	9	<9	<3	<3	<3	<3	<3	20	<3	21	<3	<3
BDE 154	0.05	0.22	1	22	<0.22	3	56	9	0.22	<0.05	340	2	126	1.4	2.7
BDE 153	0.8	2	35	13	4	16	18	2	<0.8	<2	870	5	635	4	3
BDE 138	0.3	1	1	20	2	<0.3	13	42	<0.3	<0.3	50	<0.3	58	<0.3	<1
BDE 183	0.7	2	<0.7	<0.7	<0.7	<0.7	<2	<2	<0.7	<0.7	1900	4	1700	<0.7	3.5
BDE 209	6	20	92	84	92	58	610	<6	<6	<6	12000	55	6650	26	1138
ΣPBDEs			197	467	153	88	723	63	1.3	2	17800	105	10650	42	1185
DBDPE	13	30	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13	<13
HBB	5	15	<15	<15	<15	<5	<5	<5	<5	<5	250	<5	50	<5	<5
TBB	10	40	<40	<10	<10	<10	<10	<10	50	<10	<10	124	<10	<10	<10
BTBPE	0.24	1	8	3	5	8	34	7.2	<1	<1	300	14	1990	4	4
TBPH	5	15	72	32	53	<5	<5	<5	<5	<5	45	290	290	<5	159
ΣNBFRs			94	44	60	8	34	7.2	50	--	600	427	2325	4	163

*< xx: below the respective LOQ or LOD



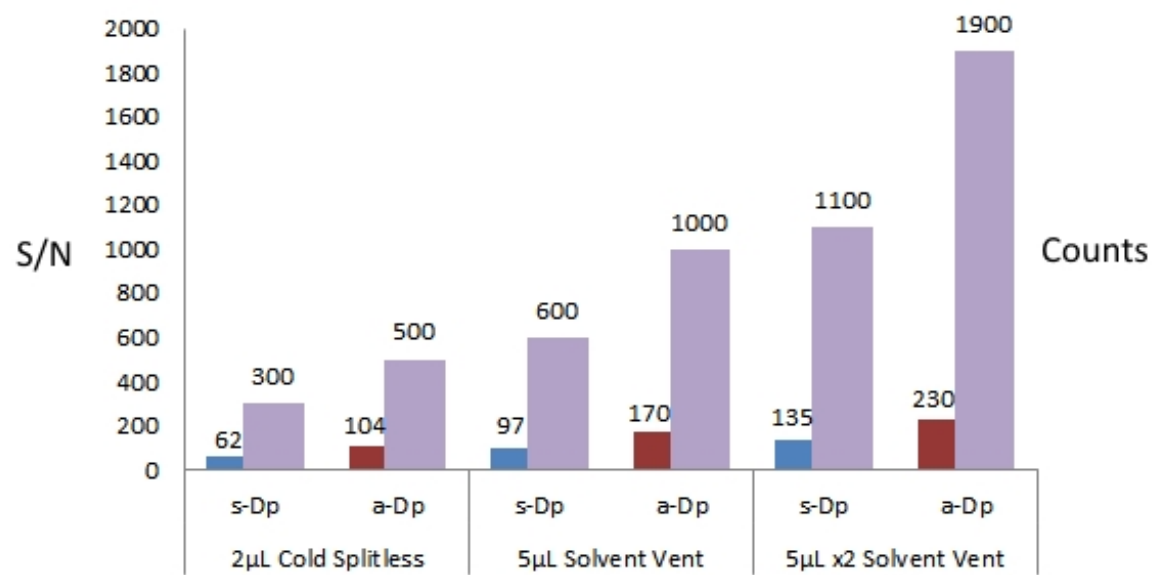
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341 **FIG 1.**



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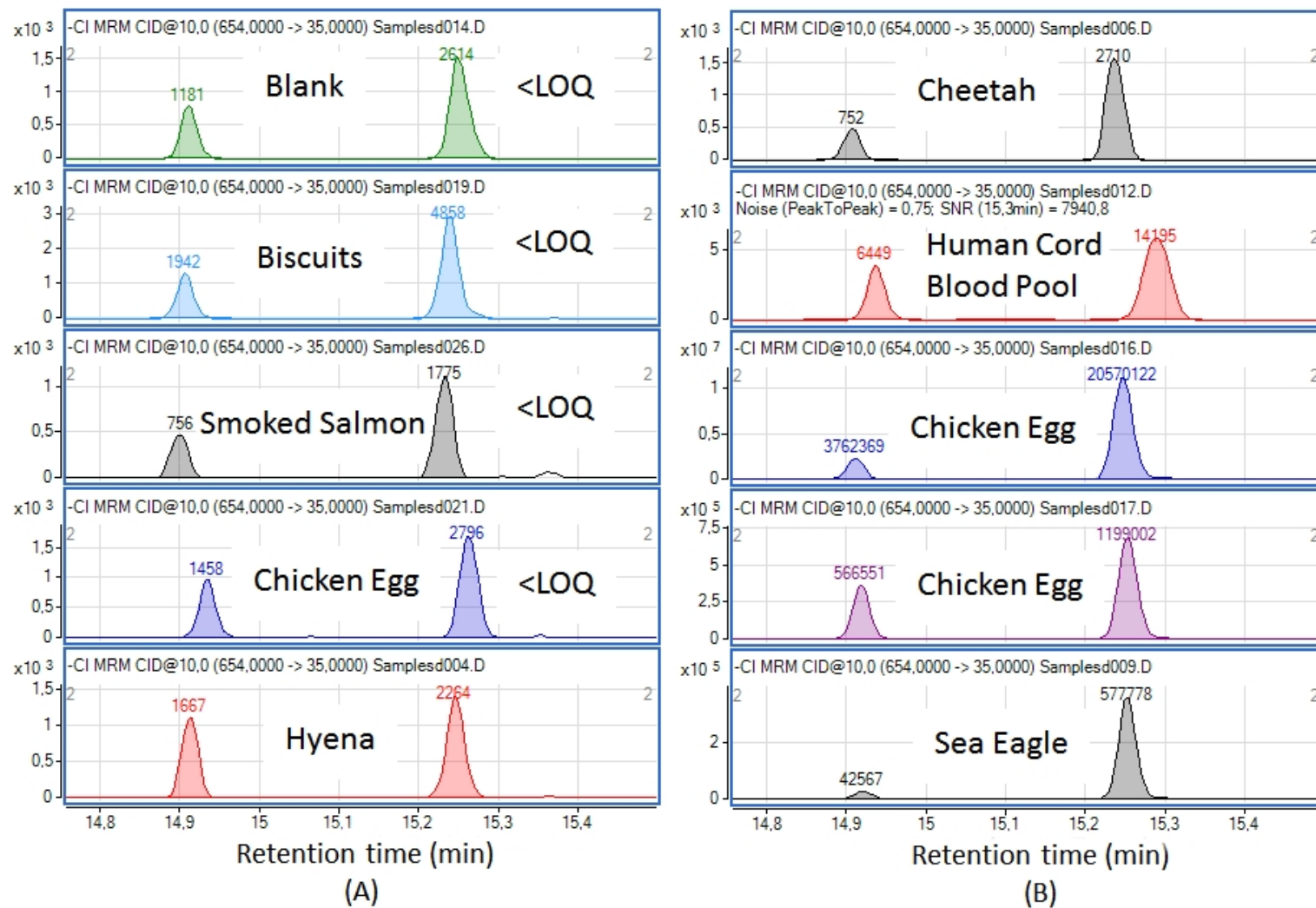
343 FIG 2

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345
346 **FIG 3.**

Absolute Signal



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348 **FIG 4**
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