Simultaneous determination of dechloranes, polybrominated diphenyl ethers and novel brominated flame retardants in food and serum

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Abstract

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

Keywords

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

1. Introduction

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

There is a large amount of literature regarding the analysis of PBDEs and novel brominated flame retardants (NBFRs) by gas chromatography–mass spectrometry (GC-MS) and GC-MS/MS using electron capture negative ionization (ECNI) and electron ionization (EI) [9]. More recently, atmospheric pressure chemical ionization (APCI) [10, 11] has also been reported for the analysis of brominated FRs. Both ECNI and APCI offer good sensitivity when compared to EI, while the specificity when using APCI and EI in MS/MS experiments is higher than the obtained by monitoring bromide ions in ECNI [10]. For the determination of Dechloranes, the majority of studies performed so far used EI-MS(/MS), with insufficient detection limits in some cases [12, 13] or ECNI-MS(/MS) with the need of an additional injection, separated from PBDEs [14–16]. GC-EI-MS/MS methods monitor transitions derived from the molecular ion to m/z 237 and m/z 228 [16]. Similar to PBDEs, the analysis of DPs can benefit of selecting more specific transitions coming from the molecular ion by using softer ionization sources. DP isomers constitute a special case study, as they have quite a particular fragmentation behaviour. Several studies have investigated the different fragmentation of *anti*- and *syn*- DP isomers under variable ECNI source temperatures, either in full-scan [17] or in SIM experiments [15], but not yet in MRM experiments.

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

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

2. Materials and methods

2.1. Chemicals and reagents

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

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

2.2 Sample Treatment

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

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

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

The chromatographic analysis was performed using an Agilent 7890B gas chromatograph, equipped with an Agilent 7693A autosampler with Multimode Inlet (MMI), coupled to a triple quadrupole mass spectrometer, 7000C (Agilent Technologies Inc., Palo Alto, CA, USA), with a CI source working in electron capture negative ionization mode. Methane was used as reagent gas at a flow of 2 mL min^{-1}. The GC separation was performed using a fused silica a ZB-semivolatiles capillary column (5% phenylarylene-95% dimethyl-polysiloxane) with a length of 20 m x 0.18 mm ID and a film thickness of 0.18 µm (Phenomenex, Torrance, CA, USA) working at a ramped flow from 1 mL min^{-1} (14 min) with 10 mL min^{-1} to 2 mL min^{-1} (10.9 min) of helium (99.999 %; Air Liquide, Liège, Belgium). The oven program was 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 total run time of 25 min. The injection of 2 µL of sample extracts was performed in cold pulsed splitless mode with at a temperature of 80 °C and a pulse time of 1.25 min. The pulse pressure was set to 50.0 psi, with a split purge flow of 50 mL min^{-1} and purge time of 1.25 min.

3. Results and discussion

3.1. MS optimization

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

The source temperature was also optimized pursuing the maximum response for every analyte. Previous studies, [17] and [15], demonstrated that low source temperatures favour the detection of the molecular ion cluster, while higher temperatures (250 °C) had different effects on both isomers. According to De la Torre et al [17], a temperature of 150 °C provided similar spectra for both isomers, with the most abundant cluster being the one corresponding to the molecular ion [M]-. However, at 250 °C, the two isomers showed a different pattern. In the case of *syn*-DP, the cluster corresponding to the ion $[M-6Cl]^-$ became the most abundant. Summarizing, higher temperature source provided more energy, hence favouring the dissociative electron capture process and increasing the abundance of fragment ions, whereas lower temperatures enhanced molecular ion abundance.

Accordingly, after obtaining low collision energies as the optimal for the determination of DPs, we theorized that low source temperatures might enhance the formation in the ion source of the parent ions for the DPs transitions. Hence, source temperatures of 250 °C, 225 °C, and 200 °C were tested. An increase in the response of DPs was seen at lower source temperatures **(Figure 2)**, while too low temperatures could affect the sensitivity for PBDEs, for which detection relies in the fragmentation to the bromide ion *m/z* 79. The temperature of 200 °C was hence chosen as a compromise for these experiments. Selected quantification and qualification transitions and ions for each analyte are summarized in **Table 1**. These findings add to the previous studies on the behaviour of DPs at different source temperatures, as in MRM experiments, the formation of an abundant molecular pattern to be selected as a parent ion, has been proved more sensitive than a high in-source fragmentation, which leads to larger losses of chlorine atoms before entering in the first quadrupole.

3.2. Analytical parameters

To maximize the signal obtained for each analyte, the use of the multimode inlet in large volume injection mode was considered. The possibility of starting at a low inlet temperature allowed the injection of a higher volume of extract. Therefore, several injection configurations were tested: cold pulsed splitless (2 µL), and solvent vent (5 µL, 2 x 5 µL and 3 x 5 µL). **Figure 3** highlights the response enhancement for the DP congeners when working at the three selected working conditions. Although solvent vent injections enhance the sensitivity for DPs as well as for the rest of the selected compounds, reproducibility and overloading issues were noticed when injecting extracts from fatty matrices, so the injection of 2 µL in cold pulsed splitless mode was selected as optimal. To test the reliability of the method, the repeatability of absolute area was studied in five repeated injections of standards at five different levels (20 fg μL^{-1}, 100 fg μL^{-1}, 1 pg μL^{-1}, 20 pg μL^{-1} and 100 pg μL^{-1}). The relative standard deviation was below 5%. Linearity of the relative response of the different compounds (to their ^{13}C isotopically labelled or BDE internal standards) was studied by analyzing standard solutions, in triplicate (five levels), in the range of 20 fg µL^{-1} to 100 pg µL^{-1}. The correlation coefficients (r^2) were higher than 0.99 for every compound, with residuals lower than 2%. Special attention has to be paid to the method sensitivity for DPs, which can be derived from **Figure 2** (injection of a 16 fg µL^{-1} standard solution in isooctane). Instrumental limits of detection (iLODs) were calculated as the lowest concentration level giving a signal-to-noise ratio (S/N) of 3. These iLODs were determined to be around 1 fg µL^{-1} for *syn*-DP and 0.5 fg µL^{-1} for *anti*-DP, when injecting 2 µL in cold pulsed splitless mode. The iLODs were even lower when using solvent vent mode, as can be seen in **Figure 3**. Obtained iLODs are summarized in **Table 1.** LODs and LOQs in real samples were estimated using the same criteria, by extrapolation from the lowest responses (detectable and quantifiable) of every compound within the analysed samples. These results are relevant especially for DP isomers, as their LODs and LOQs have been lowered sensibly in comparison to previous studies. **Table 2** lists the majority of previous studies performed to detect and quantify DP isomers, indicating the systems used and the achieved performance in each case in terms of LOD and LOQ.

3.3. Analysis of real samples

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

Special emphasis was made on the capability of the methodology to detect DPs in most of analysed samples. Due to the presence of these compounds in the procedural blanks, only the samples with DPs relative area higher than 10 times their corresponding relative area in the blank were quantified. The most remarkable results to highlight are: a pool of four cord blood human serum samples with 0.13 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*-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 serum sample with 0.33 pg g^{-1} of *syn*-DP. Dec-603 and Dec-602 were also quantified in human/animal serum ranging from 5 to 66 pg g^{-1}. Chromatograms with the quantification transition of DP isomers in the mentioned samples can be seen in **Figure 4** (**4A** for a procedure blank, biscuits, smoked salmon, chicken egg and hyena extracts, and **4B** showing a cheetah serum, human cord blood (pool), sea eagle serum, and two chicken egg extracts). **Table 3** summarizes the concentration found for each analyte in the samples.

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

4. Conclusions

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

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

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Conflict of interest

The authors declare that they have no conflict of interest.

Figure Captions

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

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

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

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

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

Compounds	RT	Q	q	iLOD (fg µL^{-1})		
				2 µL	**5 µL SV**	**10 µL 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

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)	$[M-C_{13}H_{12}Cl_6]^{+\cdot}$; 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]

n.a. – not available

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

Compounds	LOD (pg g^{-1})	LOQ (pg 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
ΣDPs			<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

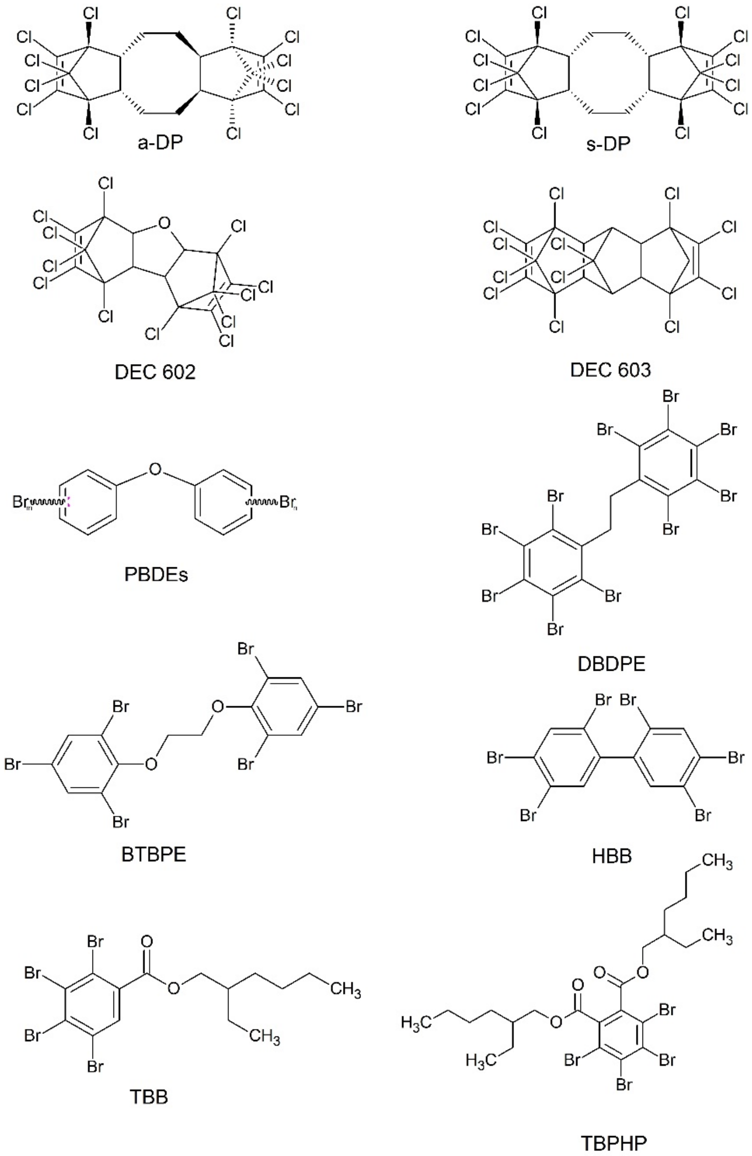

FIG 1.

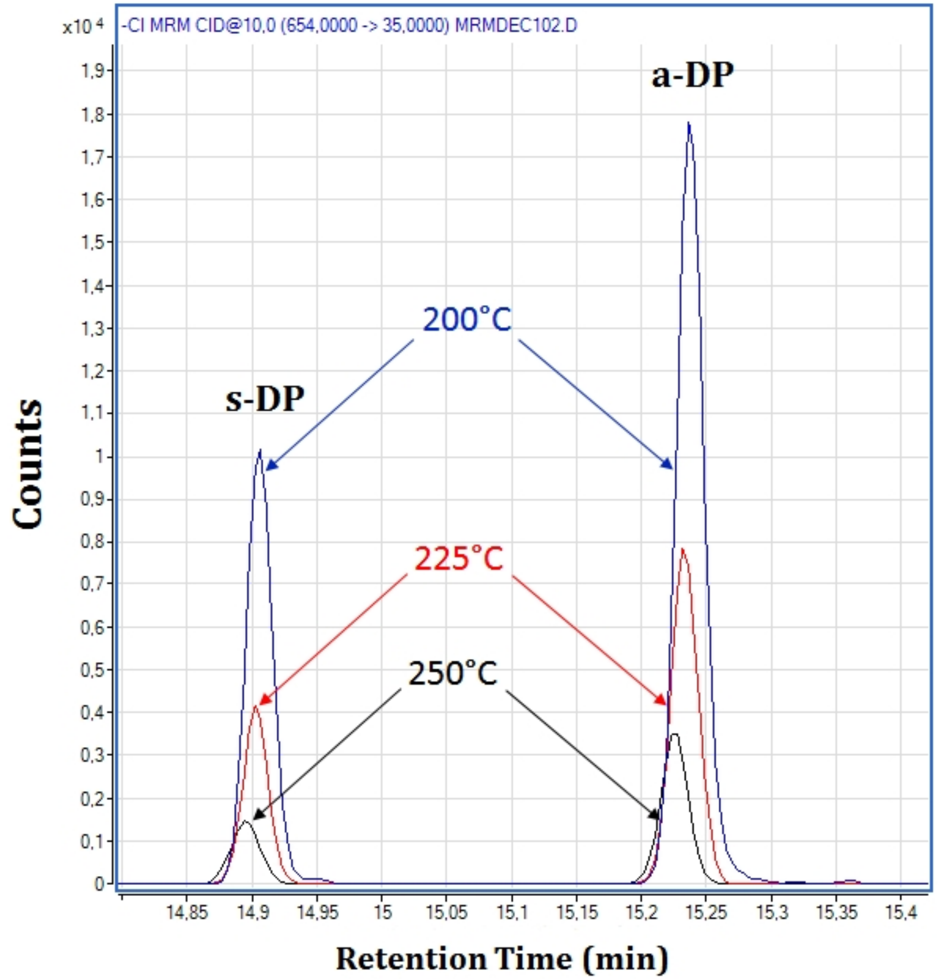
-CI MRM CID@10,0 (654,0000 -> 35,0000) MRMDEC102.D
x10 4
a-DP
s-DP
200°C
225°C
250°C
Counts
Retention Time (min)

FIG 2

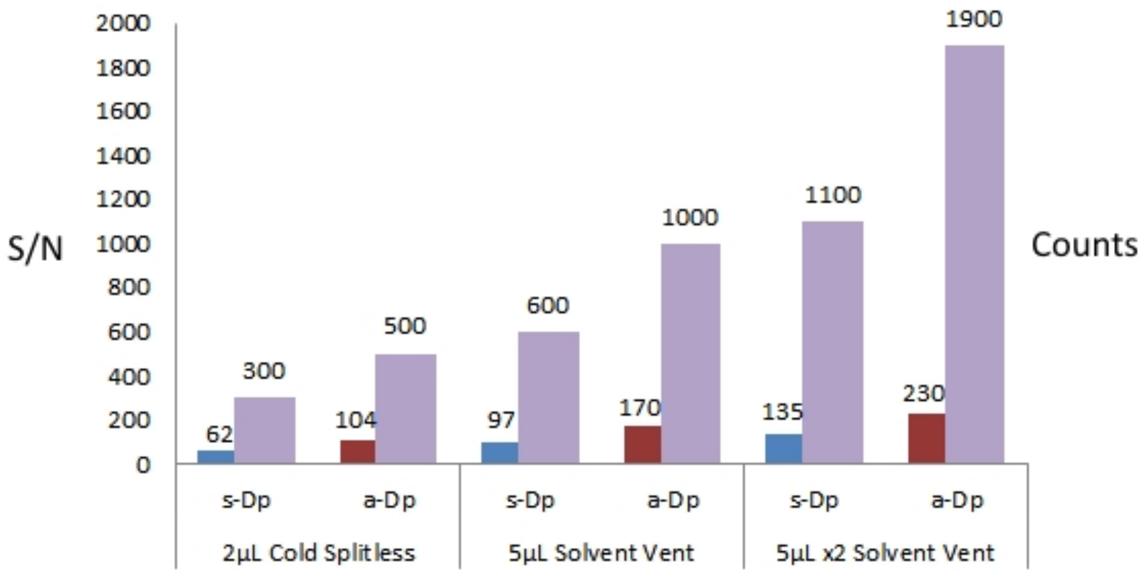
S/N
Counts
2000
1800
1600
1400
1200
1000
800
600
400
200
0
62
300
104
500
97
600
170
1000
135
1100
230
1900
s-Dp
a-Dp
s-Dp
a-Dp
s-Dp
a-Dp
2µL Cold Splitless
5µL Solvent Vent
5µL x2 Solvent Vent

FIG 3.

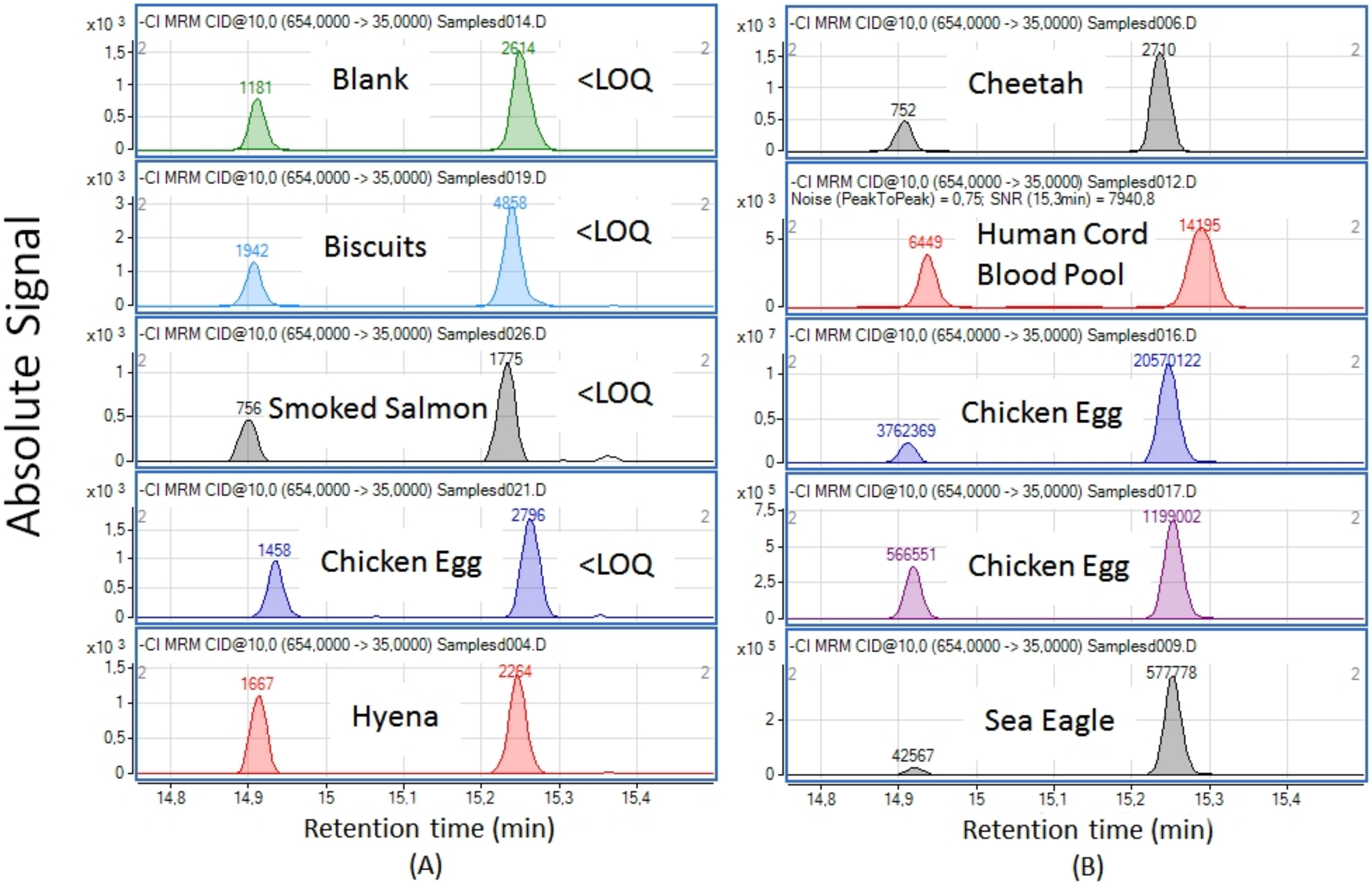
Absolute Signal
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd014.D
Blank
<LOQ
1181
2614
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd019.D
Biscuits
<LOQ
1942
4858
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd026.D
Smoked Salmon
<LOQ
756
1775
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd021.D
Chicken Egg
<LOQ
1458
2796
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd004.D
Hyena
1667
2264
Retention time (min)
(A)
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd006.D
Cheetah
752
2710
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd012.D
Noise (PeakToPeak) = 0,75; SNR (15,3min) = 7940,8
Human Cord
Blood Pool
6449
14195
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd016.D
Chicken Egg
3762369
20570122
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd017.D
Chicken Egg
566551
1199002
-CI MRM CID@10,0 (654,0000 -> 35,0000) Samplesd009.D
Sea Eagle
42567
577778
Retention time (min)
(B)

FIG 4