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# Pulsed Large Volume Injection Gas Chromatography Coupled with Electron-Capture Negative Ionization Quadrupole Mass Spectrometry for Simultaneous Determination of Typical Halogenated Persistent Organic Pollutants

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A pulsed large-volume injection gas chromatography coupled with electron-capture negative ionization quadrupole mass spectrometry (pLVI-GC/ECNI-qMS) was developed for the simultaneous determination of typical halogenated persistent organic pollutants (H-POPs). By monitoring the characteristic ions of large mass-to-charge ratio ( $m/z$ ) for each of the H-POPs rather than the chlorine and/or bromine ions, this method avoided the possible interferences arising from the H-POPs themselves and from complex matrices encountered frequently in current GC/qMS methods; and allowed, on the other hand, the use of  $^{13}\text{C}$ -labeled and perdeuterated analogues as internal standards for reliable quantification. pLVI up to 120  $\mu\text{L}$  improved the instrumental detection limits down to  $\text{pg}\text{-fg mL}^{-1}$ , comparable to or lower than those obtained by the recognized GC/high-resolution MS methods reported so far. The H-POPs including 12 polybrominated diphenyl ethers, 1 polybrominated biphenyl, 10 polychlorinated biphenyls (PCBs), 4 hexachlorocyclohexane isomers, and hexachlorobenzene were involved in this study. The method developed demonstrated good linearity ( $r^2 = 0.9904\text{--}0.9999$ ) within 0.5 to 50,000  $\text{pg mL}^{-1}$  for PCBs and 0.05 to 5000  $\text{pg mL}^{-1}$  for other H-POPs, and was satisfactory in terms of both repeatability (0.07%–2.2%) and reproducibility (2.1%–8.4%). It was validated by analyzing a NIST standard reference material SRM-1946 of Lake Superior fish tissue with low 0.01 to 63  $\text{pg g}^{-1}$  method detection limits, and successfully applied to the determination of the H-POPs in five reference materials of different matrices. (J Am Soc Mass Spectrom 2007, 18, 1375–1386) © 2007 American Society for Mass Spectrometry

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Over the past few decades, the presence of many man-made halogenated persistent organic pollutants (H-POPs) in the environment have attracted increasing public concern due to the information emerging concerning their persistence, bioaccumulation, and potential risks to human health [1]. Consequently, analytical methodology and strategies for measuring quite a variety of H-POPs classes in environmental and biological samples have been developed rapidly, generally including the procedures from sample collection, pretreatment, and extraction, to cleanup and determination [2, 3]. Organochlorinated pesticides (OCPs), such as hexachlorocyclohexane (HCHs) and hexachlorobenzene (HCB), polychlori-

nated biphenyls (PCBs), polybrominated biphenyls (PBBs), and polybrominated diphenyl ethers (PBDEs) are typical H-POPs. These various classes of contaminants are often present together in the same environmental or biological matrices, coextracted from the same sample, isolated in the same fractions, and even coeluted and/or overlapped from chromatographic systems because of their similarities in molecular structure and physicochemical behavior. From an environmental point of view, simultaneous determination of the H-POPs in environmental samples to allow comparative evaluation and comprehensive documenting is attractive [4].

Major problems in the simultaneous determination of the H-POPs in environmental and biological samples are intra- and interferences caused by the numerous congeners of similar physicochemical properties in each and/or different classes, as well as the interference

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caused by complex matrices. Additionally, the H-POPs, particularly PBDEs, often occur in the environment at extremely low levels [5]. Thus, determination methods with both high selectivity and high sensitivity are demanded. Capillary gas chromatography coupled with an electron capture detector (GC/ECD) and/or mass spectrometry (GC/MS) has been used commonly for the identification and quantification of OCPs, PCBs, PBBs, and PBDEs [6–9]. GC/ECD, a technique offering high sensitivity for the electron-capturing H-POPs, was widely used at an early stage for analyzing OCPs. However, GC/MS is preferred now because absolute chromatographic separation for the individual analyte was difficult even if multidimensional GC was employed [10]. Several GC/MS methods have been established based on high-resolution magnetic-sector MS (HR-MS) [11], tandem MS (MS/MS) using an ion trap detector [12–14], or triple quadrupole analyzer [15] and time-of-flight MS (TOF-MS) [16], as well as low-resolution quadrupole MS (qMS) [17]. Obviously, HR-MS is the most powerful tool offering high selectivity with satisfactory sensitivity by virtue of its high ultimate resolving power and accurate mass measurement; nevertheless, nowadays only a few laboratories can afford this instrument. Alternatively, MS/MS and TOF-MS provide comparable selectivity at a relatively lower cost compared with HR-MS [18]. Due to the advantages of low cost and sufficient sensitivity, qMS is commonly available in current analytical laboratories despite the relatively lower selectivity, which results from its limited resolution ability. Both ionization modes of electron impact (EI) and electron-capture negative ionization (ECNI) are extensively utilized in qMS, but each has its own merits and limitations. Generally, ECNI is significantly more sensitive, while EI is more selective for the low chlorinated PCBs, PBBs, and PBDEs [19–21]. The use of  $^{13}\text{C}$ -labeled analogues as internal standards under EI ensures reliable quantification compared with ECNI [22]. Recently, strategies have been developed with respect to the determination of PBDEs to overcome the limitations of each technique. Covaci et al. [23] combined narrow-bore (0.10 mm i.d.) capillary GC/MS by using EI with large-volume injection (LVI) up to 20  $\mu\text{L}$  achieving selective determination at the low  $\text{ng g}^{-1}$  level for five major PBDEs congeners (BDE-28, 47, 99, 100, and 153) in human adipose, yet the sensitivity for the higher brominated ( $\text{Br}_{7-10}$ ) PBDEs remained insufficient. Using ECNI, Ackerman et al. [24] novelly monitored specific large mass-to-charge ratio ( $m/z$ ) fragment ions ( $[\text{M} - \text{H}_x\text{-Br}_y]^-$ ) instead of the conventional bromine ion ( $^{78.9/80.9}\text{[Br]}^-$ ), performing isotope dilution quantification of 39 PBDEs with low  $\text{ng-pg mL}^{-1}$  instrumental detection limits (IDLs).

This study aimed to develop and validate a selective and sensitive method based on the simple and popular GC/ECNI-qMS by monitoring characteristic large  $m/z$  fragment ions and using  $^{13}\text{C}$ -labeled and/or perdeuterated internal standards as well as employing a pulsed LVI (pLVI) technique for simultaneously determining

the H-POPs at trace to ultra-trace levels in complex biological and environmental samples. We targeted 28 typical H-POPs, including five OCPs ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\delta$ -HCH, and HCB), 10 PCBs (PCB-28, 52, 101, 105, 118, 138, 153, 163, 180, and 209), one PBB (PBB-153), and 12 PBDEs (BDE-28, 47, 49, 66, 85, 99, 100, 138, 153, 154, 183, and 209) in this study.

## Experimental

### Reagents and Chemicals

The target H-POPs and the  $^{13}\text{C}$ -labeled and/or perdeuterated analogues used as internal standards are listed in Table 1. All native and  $^{13}\text{C}$ -labeled standards of PBDEs, PBB, PCBs, and HCB in nonane or iso-octane solutions were purchased from Cambridge Isotope Laboratories (CIL, Andover, MA); neat HCH standards were purchased from AccuStandard (New Haven, CT), while the  $\text{D}_6$ - $\alpha$ -HCH standard in cyclohexane solution was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All standards were of at least 99% purity. All the compounds were considered toxic and potentially carcinogenic, and were handled with caution to reduce exposure to the lowest possible level. Dichloromethane and hexane (Tedia, Fairfield, OH) were of pesticide grade, and sulfuric acid ( $\text{H}_2\text{SO}_4$ , Sinic Chemical Reagent Company, SCRC) was of analytical reagent (AR) grade. Before use, anhydrous sodium sulfate ( $\text{Na}_2\text{SO}_4$ , AR, SCRC) and neutral alumina (100–200 mesh, SCRC) were extracted with dichloromethane and baked at 350  $^\circ\text{C}$  for 3 h and 600  $^\circ\text{C}$  for 24 h, respectively.

### Instrumentation

All GC/MS analysis were performed on a GCMS-QP2010 (Shimadzu, Kyoto, Japan) equipped with a quadrupole mass analyzer and three ionization sources of EI, positive chemical ionization (PCI) and negative chemical ionization. A DB-17MS capillary column of 30 m length  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness (J & W Scientific, Folsom, CA) was used to analyze all the H-POPs except for BDE-209, which was analyzed separately on a shorter DB-XLB column of 15 m length  $\times$  0.25 mm i.d.  $\times$  0.25  $\mu\text{m}$  film thickness (J & W Scientific) to reduce possible thermal degradation [25]. A deactivated guard column of 5 m length  $\times$  0.25 mm i.d. was connected before each column. The GC was equipped with a split/splitless injector and a program temperature vaporizer (PTV), the former for splitless 1- $\mu\text{L}$  injection and the latter for pLVI. For the splitless injection, the injector temperature was held at 280  $^\circ\text{C}$ , and the splitless time was 4 min for analyzing BDE-209 and 2 min for simultaneously analyzing all the other H-POPs. An AOC-20i autosampler (Shimadzu) equipped with one of three syringes with different capacity, namely 10, 50, and 250  $\mu\text{L}$ , was used to inject the samples. The GC/MS interface was maintained at

**Table 1.** The H-POPs determined and isotopically labeled internal standards, as well as their quantitative (Quant.) and qualitative (Qual.) ions in SIM mode and absolute instrumental detection limits (IDL, S/N = 3) using the four methods: GC/EI-qMS, GC/PCI-qMS, GC/ECNI-qMS with monitoring base peak ions, and GC/ECNI-qMS with monitoring characteristic ions

H-POPs		GC/ECNI-qMS															
Name	IUPAC no. or abbr.	GC/EI-qMS				GC/PCI-qMS				Monitoring base peak ions				Monitoring characteristic ions			
		Quant. m/z	Qual. m/z	IDL fg	Quant. m/z	Qual. m/z	IDL fg	Quant. m/z	Qual. m/z	IDL fg	Quant. m/z	Qual. m/z	IDL fg	Quant. m/z	Qual. m/z	IDL fg	
<b>Organochlorine pesticide (OCP)</b>																	
<sup>13</sup> C <sub>6</sub> -Hexachlorobenzene	<sup>13</sup> C <sub>6</sub> -HCB	289.8	291.8, 287.8	289.8	292.8, 288.8	792	289.8	291.8, 287.8	289.8	291.8, 287.8	0.81	289.8	291.8, 287.8	289.8	291.8, 287.8	0.81	
Hexachlorobenzene	HCB	283.8	285.8, 281.8	52.5	286.8, 282.8		283.8	285.8, 281.8		283.8		283.8	285.8, 281.8		283.8		
<b>Hexachlorocyclohexane (HCH) isomer</b>																	
D <sub>α</sub> -α-HCH	D <sub>α</sub> -α-HCH	224.8	222.8, 186.9	292	222.8, 186.9	2090	224.8	222.8, 186.9	224.8	222.8, 186.9	7.95	224.8	222.8, 186.9	224.8	222.8, 186.9	7.95	
α-HCH	α-HCH	218.8	216.8, 180.9	364	216.8, 180.9	1920	218.8	216.8, 180.9	218.8	216.8, 180.9	16.7	218.8	216.8, 180.9	218.8	216.8, 180.9	16.7	
β-HCH	β-HCH	218.8	216.8, 180.9	323	216.8, 180.9	1470	218.8	216.8, 180.9	218.8	216.8, 180.9	5.72	218.8	216.8, 180.9	218.8	216.8, 180.9	5.72	
γ-HCH	γ-HCH	218.8	216.8, 180.9	367	216.8, 180.9	2350	218.8	216.8, 180.9	218.8	216.8, 180.9		218.8	216.8, 180.9	218.8	216.8, 180.9		
δ-HCH	δ-HCH	218.8	216.8, 180.9		216.8, 180.9		218.8	216.8, 180.9	218.8	216.8, 180.9		218.8	216.8, 180.9	218.8	216.8, 180.9		
<b>Polychlorinated biphenyl (PCB) congener</b>																	
<sup>13</sup> C <sub>12</sub> -2,4,4'-TrCB	<sup>13</sup> C <sub>12</sub> -PCB-28	268.0	270.0, 198.0	117	270.0, 198.0	887	268.0	270.0, 198.0	268.0	270.0, 198.0	116	268.0	270.0, 198.0	268.0	270.0, 198.0	116	
2,4,4'-TrCB	PCB-28	255.9	257.9, 186.0	303.9	257.9, 186.0	304.9	255.9	257.9, 186.0	255.9	257.9, 186.0		255.9	257.9, 186.0	255.9	257.9, 186.0		
<sup>13</sup> C <sub>12</sub> -2,2',5,5'-TeCB	<sup>13</sup> C <sub>12</sub> -PCB-52	291.9	289.9, 219.9	162	289.9, 219.9	929	291.9	289.9, 219.9	291.9	289.9, 219.9	237	291.9	289.9, 219.9	291.9	289.9, 219.9	237	
2,2',5,5'-TeCB	PCB-52	337.9	339.9, 265.9	176	339.9, 265.9	762	337.9	339.9, 265.9	337.9	339.9, 265.9	45.5	337.9	339.9, 265.9	337.9	339.9, 265.9	45.5	
<sup>13</sup> C <sub>12</sub> -2,2',4,5,5'-PeCB	<sup>13</sup> C <sub>12</sub> -PCB-101	325.9	327.9, 253.9	140	327.9, 253.9	852	325.9	327.9, 253.9	325.9	327.9, 253.9	83.5	325.9	327.9, 253.9	325.9	327.9, 253.9	83.5	
2,2',4,5,5'-PeCB	PCB-101	325.9	327.9, 253.9	138	327.9, 253.9	806	325.9	327.9, 253.9	325.9	327.9, 253.9		325.9	327.9, 253.9	325.9	327.9, 253.9		
2,3',4,4',5-PeCB	PCB-105	325.9	327.9, 253.9	214	327.9, 253.9	782	325.9	327.9, 253.9	325.9	327.9, 253.9		325.9	327.9, 253.9	325.9	327.9, 253.9		
2,3',4,4',5-PeCB	PCB-118	371.8	373.8, 301.9	193	373.8, 301.9	774	371.8	373.8, 301.9	371.8	373.8, 301.9	115	371.8	373.8, 301.9	371.8	373.8, 301.9	115	
<sup>13</sup> C <sub>12</sub> -2,2',3,4,4',5'-HxCB	<sup>13</sup> C <sub>12</sub> -PCB-138	359.8	361.8, 289.9	202	361.8, 289.9	782	359.8	361.8, 289.9	359.8	361.8, 289.9		359.8	361.8, 289.9	359.8	361.8, 289.9		
2,2',3,4,4',5'-HxCB	PCB-138	371.8	373.8, 301.9	193	373.8, 301.9	768	371.8	373.8, 301.9	371.8	373.8, 301.9		371.8	373.8, 301.9	371.8	373.8, 301.9		
<sup>13</sup> C <sub>12</sub> -2,2',4,4',5,5'-HxCB	<sup>13</sup> C <sub>12</sub> -PCB-153	359.8	361.8, 289.9	202	361.8, 289.9	774	359.8	361.8, 289.9	359.8	361.8, 289.9		359.8	361.8, 289.9	359.8	361.8, 289.9		
2,2',4,4',5,5'-HxCB	PCB-153	359.8	361.8, 289.9	193	361.8, 289.9	768	359.8	361.8, 289.9	359.8	361.8, 289.9		359.8	361.8, 289.9	359.8	361.8, 289.9		
<sup>13</sup> C <sub>12</sub> -3,4',5,6-HxCB	PCB-163	359.8	361.8, 289.9	202	361.8, 289.9	774	359.8	361.8, 289.9	359.8	361.8, 289.9		359.8	361.8, 289.9	359.8	361.8, 289.9		
2,3',4',5,6-HxCB	PCB-163	405.8	407.8, 335.9	197	407.8, 335.9	1170	405.8	407.8, 335.9	405.8	407.8, 335.9	5.55	405.8	407.8, 335.9	405.8	407.8, 335.9	5.55	
<sup>13</sup> C <sub>12</sub> -2,2',3,4,4',5,5'-HpCB	<sup>13</sup> C <sub>12</sub> -PCB-180	393.8	395.8, 323.9	381	395.8, 323.9	1830	393.8	395.8, 323.9	393.8	395.8, 323.9	2.25	393.8	395.8, 323.9	393.8	395.8, 323.9	2.25	
2,2',3,4,4',5,5'-HpCB	PCB-180	509.7	511.7, 507.7		511.7, 507.7		509.7	511.7, 507.7	509.7	511.7, 507.7		509.7	511.7, 507.7	509.7	511.7, 507.7		
<sup>13</sup> C <sub>12</sub> -2,2',3,3',4,4',5,5',6,6'-DeCB	<sup>13</sup> C <sub>12</sub> -PCB-209	497.6	499.6, 495.6		499.6, 495.6		497.6	499.6, 495.6	497.6	499.6, 495.6		497.6	499.6, 495.6	497.6	499.6, 495.6		
2,2',3,3',4,4',5,5',6,6'-DeCB	PCB-209						497.6	499.6, 495.6	497.6	499.6, 495.6		497.6	499.6, 495.6	497.6	499.6, 495.6		
<b>Polychlorinated biphenyl (PBB) congener</b>																	
2,2',4,4',5,5'-HxBB	PBB-153	627.5	629.5, 546.6	89.5	629.5, 546.6	1220	627.5	629.5, 546.6	627.5	629.5, 546.6	16.3	627.5	629.5, 546.6	627.5	629.5, 546.6	16.3	
2,2',4,4',5,5'-HxBB	PBB-153						627.5	629.5, 546.6	627.5	629.5, 546.6		627.5	629.5, 546.6	627.5	629.5, 546.6		
<b>Polybrominated diphenyl ether (PBDE) congener</b>																	
2,2',4,4'-TeBDE	BDE-28	405.8	407.8, 247.0	77.6	407.8, 247.0	493	405.8	407.8, 247.0	405.8	407.8, 247.0	0.38	405.8	407.8, 247.0	405.8	407.8, 247.0	0.38	
2,2',4,4'-TeBDE	BDE-47	485.7	483.7, 325.9	90.5	483.7, 325.9	897	485.7	483.7, 325.9	485.7	483.7, 325.9	0.37	485.7	483.7, 325.9	485.7	483.7, 325.9	0.37	
2,2',4,4',5-TeBDE	BDE-49	485.7	483.7, 325.9	438	483.7, 325.9	2520	485.7	483.7, 325.9	485.7	483.7, 325.9	1.37	485.7	483.7, 325.9	485.7	483.7, 325.9	1.37	
2,2',4,4',5-TeBDE	BDE-66	485.7	483.7, 325.9	146	483.7, 325.9	983	485.7	483.7, 325.9	485.7	483.7, 325.9	0.38	485.7	483.7, 325.9	485.7	483.7, 325.9	0.38	
<sup>13</sup> C <sub>12</sub> -3,3',4,4'-TeBDE	<sup>13</sup> C <sub>12</sub> -BDE-77	497.7	495.7, 499.7	275	495.7, 499.7	1030	497.7	495.7, 499.7	497.7	495.7, 499.7	0.44	497.7	495.7, 499.7	497.7	495.7, 499.7	0.44	
2,2',3,4,4',5-TeBDE	BDE-85	563.6	565.6, 403.8	139	565.6, 403.8	646.5	563.6	565.6, 403.8	563.6	565.6, 403.8	0.37	563.6	565.6, 403.8	563.6	565.6, 403.8	0.37	
2,2',4,4',5-PeBDE	BDE-99	563.6	565.6, 403.8	147	565.6, 403.8	897	563.6	565.6, 403.8	563.6	565.6, 403.8	0.36	563.6	565.6, 403.8	563.6	565.6, 403.8	0.36	
2,2',4,4',6-PeBDE	BDE-100	563.6	565.6, 403.8	188	565.6, 403.8	2410	563.6	565.6, 403.8	563.6	565.6, 403.8	0.54	563.6	565.6, 403.8	563.6	565.6, 403.8	0.54	
<sup>13</sup> C <sub>12</sub> -3,3',4,4',5-PeBDE	<sup>13</sup> C <sub>12</sub> -BDE-126	575.6	577.6, 573.6	145	577.6, 573.6	1610	575.6	577.6, 573.6	575.6	577.6, 573.6	0.32	575.6	577.6, 573.6	575.6	577.6, 573.6	0.32	
2,2',3,4,4',5-HxBDE	BDE-138	643.5	641.5, 483.6	116	641.5, 483.6	646.5	643.5	641.5, 483.6	643.5	641.5, 483.6	0.34	643.5	641.5, 483.6	643.5	641.5, 483.6	0.34	
2,2',3,4,4',5-HxBDE	BDE-153	643.5	641.5, 483.6	244	641.5, 483.6	2810	643.5	641.5, 483.6	643.5	641.5, 483.6	0.72	643.5	641.5, 483.6	643.5	641.5, 483.6	0.72	
2,2',4,4',5,6-HxBDE	BDE-154	643.5	641.5, 483.6	789	641.5, 483.6	960.1	643.5	641.5, 483.6	643.5	641.5, 483.6		643.5	641.5, 483.6	643.5	641.5, 483.6		
2,2',3,4,4',5,6-HpBDE	BDE-183	721.4	723.4, 561.6	244	723.4, 561.6	722.4	721.4	723.4, 561.6	721.4	723.4, 561.6	0.72	721.4	723.4, 561.6	721.4	723.4, 561.6	0.72	
<sup>13</sup> C <sub>12</sub> -2,2',3,3',4,4',5,5',6,6'-DeBDE	<sup>13</sup> C <sub>12</sub> -BDE-209	811.3	813.3, 793.2	89.5	813.3, 793.2	960.1	811.3	813.3, 793.2	811.3	813.3, 793.2	366	811.3	813.3, 793.2	811.3	813.3, 793.2	366	
2,2',3,3',4,4',5,5',6,6'-DeBDE	BDE-209	799.3	795.1, 961.2	789	795.1, 961.2	960.1	799.3	795.1, 961.2	799.3	795.1, 961.2		799.3	795.1, 961.2	799.3	795.1, 961.2		

**Table 2.** The MS optimization parameters and their optimal values using the four methods: GC/EI-qMS, GC/PCI-qMS, GC/ECNI-qMS with monitoring base peak ions, and GC/ECNI-qMS with monitoring characteristic ions

	Optimization parameters		Optimal values			
	Range	Interval	GC/EI-qMS	GC/PCI-qMS	ECNI-qMS <sup>a</sup>	ECNI-qMS <sup>b</sup>
Electron energy (eV)	40-80	5 <sup>c</sup> , 2 <sup>d</sup>	60 <sup>e</sup> , 70 <sup>f</sup>	55 <sup>e</sup> , 65 <sup>f</sup>	70 <sup>e</sup> , 60 <sup>f</sup>	56 <sup>e</sup> , 60 <sup>f</sup>
Filament emission current ( $\mu$ A)	30-70	5 <sup>c</sup> , 2 <sup>d</sup>	55 <sup>e</sup> , 60 <sup>f</sup>	55 <sup>e</sup> , 60 <sup>f</sup>	65 <sup>e</sup> , 60 <sup>f</sup>	50 <sup>e</sup> , 55 <sup>f</sup>
Source temperature ( $^{\circ}$ C)	150-260	10 <sup>c</sup> , 5 <sup>d</sup>	200 <sup>e</sup> , 250 <sup>f</sup>	190 <sup>e</sup> , 250 <sup>f</sup>	250 <sup>e</sup> , 250 <sup>f</sup>	195 <sup>e</sup> , 250 <sup>f</sup>
Moderating gas type	CH <sub>4</sub> , <i>i</i> -C <sub>4</sub> H <sub>10</sub>	-	-	<i>i</i> -C <sub>4</sub> H <sub>10</sub> <sup>e,f</sup>	<i>i</i> -C <sub>4</sub> H <sub>10</sub> <sup>e,f</sup>	<i>i</i> -C <sub>4</sub> H <sub>10</sub> <sup>e,f</sup>
Moderating gas pressure (10 <sup>-3</sup> Pa)	2.0-5.0	0.5 <sup>c</sup> , 0.1 <sup>d</sup>	-	3.5 <sup>e</sup> , 2.5 <sup>f</sup>	2.5 <sup>e</sup> , 2.0 <sup>f</sup>	3.6 <sup>e</sup> , 3.2 <sup>f</sup>

<sup>a</sup>With monitoring of base peak ions.<sup>b</sup>With monitoring of characteristic ions.<sup>c</sup>Under EI and PCI.<sup>d</sup>Under ECNI.<sup>e</sup>For simultaneously analyzing all the H-POPs except BDE-209.<sup>f</sup>For analyzing the BDE-209 separately.

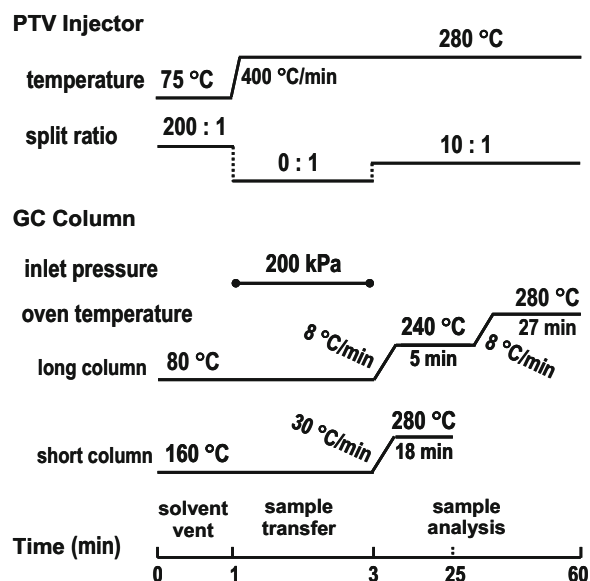
280  $^{\circ}$ C. Helium (He, 99.999%, Linde, Xiamen, China) was used as the GC carrier, and methane (CH<sub>4</sub>, 99.995%, Linde) and isobutane (*i*-C<sub>4</sub>H<sub>10</sub>, 99.99%, Linde) were used as the reagent gas and moderating gas in PCI and ECNI modes, respectively.

#### pLVI-GC/ECNI-qMS with Monitoring of Characteristic Ions

GC/EI-qMS, GC/PCI-qMS and GC/ECNI-qMS were compared in their selectivity and sensitivity for analyzing the H-POPs. In each ionization mode, full scan mass spectra were recorded for each of the H-POPs, and the MS parameters of electron energy, emission current, ionization temperature, the type and pressure of reagent gas for PCI, and moderating gas for ECNI were optimized, as listed in Table 2, in a random sequence for maximum instrumental sensitivity. The optimization experiments were undertaken using 1- $\mu$ L splitless injection of BDE-209 standard solution or mixed standard solution containing all the other H-POPs, and an amount 10 to 40 times higher than the IDL for a given compound was employed. Under optimal conditions, a five-point internal calibration curve was established for each of the H-POPs and the lowest calibration standard was repeatedly injected 11 times to obtain the standard deviation (SD) for determining the IDL for each of the H-POPs.

pLVI was carried out by pulsed injections (12 s per injection) with the autosampler, and the PTV was operated in solvent vent mode. The maximum allowable sample introduction volume (employing hexane as solvent) for pLVI was initially determined by injecting the same amounts of the H-POPs in different volumes, followed by optimizing a number of PTV parameters, such as sample volume per injection, split ratio, initial and final PTV temperature, as well as column inlet pressure during the sample transfer. The optimum PTV parameters were determined based on the requirement that, for each analyte, the mean injection efficiency and repeatability of 11 successive injections must be com-

parable to the 1- $\mu$ L splitless injection, and that the decomposition of thermally labile components was insignificant. As illustrated in Figure 1, 120  $\mu$ L was introduced onto the column by six pulsed injections of 20  $\mu$ L each at an initial temperature of 75  $^{\circ}$ C with the split valve open; between adjacent injections, the hexane was evaporated selectively and eliminated via the split vent at the split ratio of 200:1, while the analytes were retained on the packing material (8 mg silanized quartz wool) in the liner (straight tube design, 1.2 mm i.d.  $\times$  9.5 cm length, deactivated using dimethyldichlorosilane) by cold trapping. After sample injection and solvent evaporation, the split valve was closed (split ratio = 0:1) and the PTV rapidly heated up to the final temperature of 280  $^{\circ}$ C for transferring the analytes



**Figure 1.** Parameters of the PTV temperature and split ratio as well as the GC column inlet pressure and oven temperature during solvent vent (0–1 min), sample transfer (1–3 min), sample analysis (3–25 min for BDE-209, and 3–60 min for the other all H-POPs).



under a pulsed high-pressure of 200 kPa. Once the analyte transfer was finished, the split valve was opened at the split ratio of 10:1 to vent the nonvolatile matrix components. In general, the liner and silanized quartz wool were changed after 500 injections of standards and 100 injections of sample extracts, respectively.

The proposed pLVI-GC/ECNI-qMS was then evaluated. Linearities were determined by creating six-point calibration curves at concentrations of 0.05, 0.5, 5, 50, 500, and 5000  $\text{pg mL}^{-1}$  for the PBDEs, PBB-153, and OCPs, and 0.5, 5, 50, 500, 5000, and 50,000  $\text{pg mL}^{-1}$  for the PCBs. IDLs for the H-POPs were determined as the concentration corresponding to three times the SD of 11 measurements of the lowest calibration standard. Repeatability was determined by 11 successive injections of the lowest calibration standards, and reproducibility was determined by seven injections each time, once every two days within two weeks.

### Samples and Pretreatment

A standard reference material (SRM 1946) of Lake Superior fish tissue was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD) for assessing method accuracy. Two grass carp were purchased from a local market to prepare method blank sample. The grass carp samples were ground and homogenized, Soxhlet extracted for 24 h, and then ultrasonically extracted three times using a dichloromethane/hexane (vol/vol = 1/1) mixture. After confirmation that the final extracts concentrated contained neither the analytes nor chromatographic interferences, the fish tissues obtained were used as method blank samples. Five reference materials of clean soil (EDF-5183), heavily contaminated sediment (EDF-5184), clean fish (EDF-2524, Pacific herring), contaminated fish (EDF-2525, Lake Ontario lake trout) and fortified fish (EDF-2526, Sockeye salmon) were purchased from CIL to determine the H-POPs, our laboratory being one of the participating laboratories of the second round of international laboratory study organized by CIL and Cerilliant Corporation from May to August, 2006.

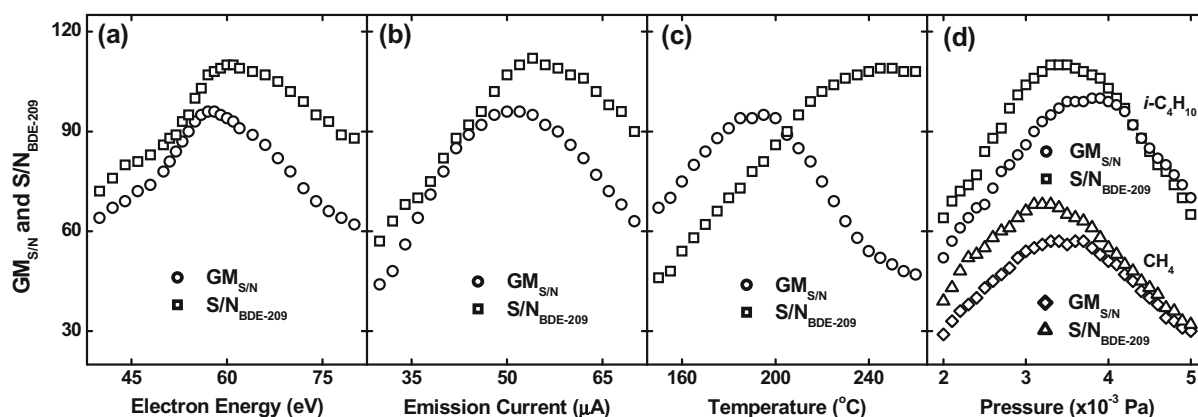
The SRM-1946 fish tissue was analyzed in two batches at an interval of 4 months. Each aliquot of 0.5 g fish tissue (wet weight) was mixed with 15 g  $\text{Na}_2\text{SO}_4$  and wrapped into a clean filter paper. After spiking with the internal standards, the samples were Soxhlet extracted with a dichloromethane/hexane (vol/vol = 1/1) mixture for 24 h, throughout which time the container was wrapped with aluminum foil to minimize possible photodegradation of the analytes, particularly BDE-209. The resultant extract was reduced to 15 mL using a rotary evaporator, and further to  $\sim 1$  mL using nitrogen ( $\text{N}_2$ ) stream, followed by solvent exchange into 5 mL hexane. The extract then had 5 mL concentrated  $\text{H}_2\text{SO}_4$  added and was shaken for 5 min to destroy most of the lipids.

After centrifugation, the upper hexane was decanted and then concentrated to 1 mL and loaded onto an alumina column (1.0 cm i.d.  $\times$  30 cm length) packed with 10 g deactivated neutral alumina for further cleanup. The first eluate of 10 mL hexane was discarded, while the second fraction of 30 mL dichloromethane/hexane (vol/vol = 1/1) was collected, then concentrated under a  $\text{N}_2$  stream and solvent exchanged into 0.5 mL hexane. Each batch comprised five replicate samples ensuring analysis precision, a method blank sample, and a spiked method blank sample for checking sample contamination and losses during sample pretreatment. The method determination limits (MDL) for the H-POPs were determined from spiked method blank samples: method blank samples spiked with the corresponding standards at a concentration of about 5 to 10 times the signal to noise ratio (S/N). Seven replicates of the spiked method blank samples were analyzed using the same procedures described above, and the MDL of each H-POP determined was calculated as the average method blank value plus 10 times the SD. The soil, sediment, and fish reference material samples were each analyzed in one batch comprised five replicates; their pretreatment procedures were the same as the SRM fish tissues described above.

## Results and Discussion

### Comparison of EI-qMS, PCI-qMS, and ECNI-qMS for determination of the HOPs

Mass spectra of the H-POPs strongly depend on the type of ionization source. EI mass spectra are characterized by relatively abundant fragment ions, which offer more information on the molecular structures, while PCI and ECNI mass spectra are simpler. In the EI mass spectra, molecular ions ( $[\text{M}]^+$ ) are the base peak ions for all the H-POPs with the exception of HCHs, which fragment ions  $[\text{M} - \text{Cl}_{2,3,5}]^+$  are base peak ions. In the PCI mass spectra, protonated molecular ions ( $[\text{MH}]^+$ ) are the base peak ions for all the HOCs except for the fragment ions  $[\text{MH} - \text{Cl}_2]^+$  for HCHs. The ECNI mass spectra of HCB and highly chlorinated PCBs (containing more than four chlorine atoms) exhibited dominating molecular ions ( $[\text{M}]^-$ ) as the base peak ions, while those of the HCHs showed strong to moderate fragment  $[\text{Cl}]^-$ ,  $[\text{HCl}_2]^-$ , and  $[\text{M} - \text{HCl}]^-$  ions. Nevertheless, the ECNI mass spectra of the lower chlorinated PCB-28 and 52 as well as PBB-153 and PBDEs yield predominant  $[\text{Cl}]^-$  and  $[\text{Br}]^-$ , respectively, but weak  $[\text{M}]^-$ . Exceptionally, the ECNI mass spectra of BDE-209 showed intense to moderate  $[\text{C}_6\text{Br}_5\text{O}]^-$ ,  $[\text{C}_6\text{Br}_4\text{O}]^-$ , and  $[\text{Br}]^-$  agreeing with the findings of previous investigators [26]; besides,  $[\text{M} - \text{Br}_{1-5}]^-$  due to the subsequent losses of bromine atoms from the  $[\text{M}]^-$  were observed in low 1.3% to 17% abundance with the expected isotopic pattern.



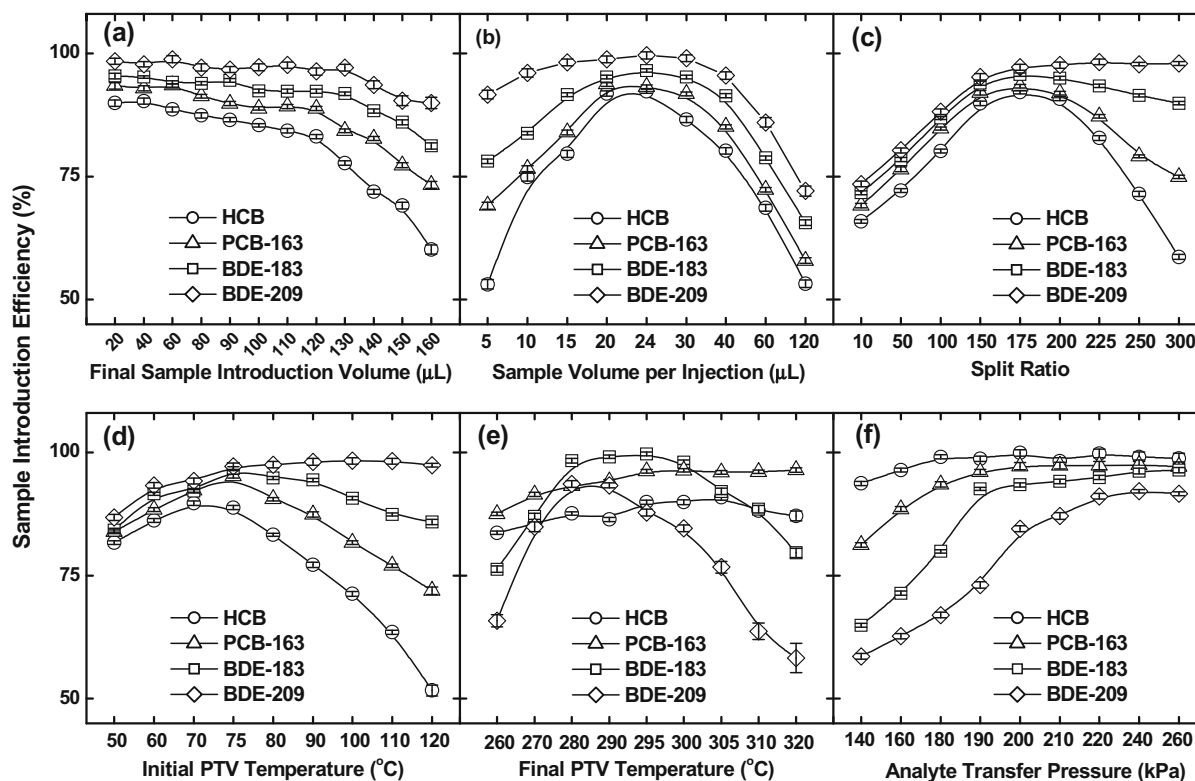
**Figure 2.** Geometric mean of the signal-to-noise ratios ( $S/N$ ) for the quantitative ions (see Table 1) of all the H-POPs except BDE-209 ( $GM_{S/N}$ ) and the  $S/N$  for the quantitative ion of BDE-209 ( $S/N_{BDE-209}$ ) as functions of electron energy (eV) (a), filament emission current ( $\mu A$ ) (b), ion source temperature ( $^{\circ}C$ ) (c), and pressure ( $\times 10^{-3}$  Pa) of  $i-C_4H_{10}$  and  $CH_4$  (d).

The quantitative and qualitative ions selected for the H-POPs under each ionization mode are listed in Table 1. In EI and PCI modes, the molecular and large- $m/z$  fragment ions, which were both structurally characteristic and most abundant, were unquestionably selected. In the ECNI mode, two groups of quantitative and qualitative ions were selected because the most abundant ions were not all structurally characteristic for the H-POPs studied. For example, the major  $[Br]^-$  of almost all the PBDEs, PBB-153, and the major  $[Cl]^-$  of the PCB-28, 52 only reflected the element composition of  $^{78.9/80.9}Br$  and  $^{35.0/37.0}Cl$  but no information on the molecular structure. In this case, either the base peak ion or the characteristic ion may be monitored with different preference to sensitivity or selectivity. Monitoring base peak ions was relatively sensitive but might produce false identification; whereas, monitoring characteristic ions suffered considerable losses in sensitivity although it achieved much better selectivity. As can be seen in Table 1, the absolute IDLs of  $\gamma-HCH$ , PCB-52, BDE-138, and PBB-153 were 16.7, 237, 0.54, and 16.3 fg, respectively, when their corresponding base peak ions were monitored, while the IDLs were 193, 9110, 104, and 29.8 fg, respectively, when monitoring the corresponding characteristically higher  $m/z$  ions.

The optimized ionization conditions of EI, PCI, and ECNI for monitoring the base peak ions and/or the characteristic ions (listed in Table 1) when simultaneously analyzing all the H-POPs except BDE-209 and when separately analyzing the BDE-209 are given in Table 2. The ECNI mass spectra of the H-POPs were observed to be strongly dependent on the qMS operation conditions of electron energy, filament emission current, ion source temperature, the type of moderating gas, and pressure. Generally, the  $S/N$  ratios of the characteristic ions of high  $m/z$  (listed in Table 1) were improved by factors of approximately one order of magnitude after optimization (see Figure 2). For example, the relative abundance of  $[M - HBr]^-$  ( $m/z = 561.6, 563.6$ ) for BDE-138 was improved from 0.8% to 24%. Results suggested that lower electron

energy, emission current, ion source temperature, and higher moderating gas pressure facilitated the production of thermal electrons, thus forming more  $[M]^-$  (for HCB, PCBs, PBB) through a resonance thermal electron capture process or high- $m/z$  fragment ions ( $[M - HBr]^-$  for PBDE<sub>n=3-7</sub>,  $[M - HCl]^-$  for HCHs, and  $[M - 3Br]^-$  for BDE-209) through a dissociative resonance electron capture process [27]. Besides, a higher pressure of moderating gas increased the frequency of collision and stabilization of these ions formed. However, extremely low electron energy and emission current decreased the ionization efficiencies, and too much moderating gas hampered the transfer of the ions from the ion source to the quadrupole analyzer; hence, the absolute intensities of the ions were actually reduced. In addition, the results indicated that the optimum pressure using  $i-C_4H_{10}$  as moderating gas was slightly lower than that using  $CH_4$  as moderating gas for obtaining a comparable sensitivity.

Comparison of the IDLs between the four GC/qMS-based methods (Table 1) shows that the GC/ECNI-qMS was the most sensitive for all the H-POPs when the base peak ions were monitored for quantification. Comparatively, the GC/ECNI-qMS with monitoring the characteristic ions were 1 to 200 times less sensitive for the majority of the H-POPs studied, and the sensitivity generally increased along with the increase in the number of Cl or Br substitutions in the molecules. For example, IDL of ECNI with monitoring the characteristic  $[M - HBr]^-$  for BDE-28 containing 3 Br atoms was 9526 times higher than that with monitoring the  $[Br]^-$ . This is because the dissociative electron capture dominates the ionization processes of PBDEs, producing primarily  $[Br]^-$ ; additionally, the formation enthalpies of PBDE congeners decrease with the decreasing number of bromines [28]. The IDLs of the GC/EI-qMS were  $\sim 1$  to 600 times less sensitive than those of the GC/ECNI-qMS when monitoring the base peak ions, while those of the GC/PCI-qMS were 4 to 15 times less sensitive than the GC/EI-qMS.



**Figure 3.** Sample introduction efficiency and repeatability (SD,  $n = 11$ , shown as error bars), of the pLVI for HCB, PCB-163, BDE-183, and BDE-209 as a function of final sample introduction volume (a), sample volume per injection (b), split ratio (c), initial PTV temperature (d), final PTV temperature (e), and sample transfer pressure (f).

When analyzing a real sample, selectivity predominance over sensitivity, in terms of many possible chlorinated and/or brominated chromatographic interferences, have been reported, including the naturally-occurring compounds that vary from matrix to matrix and sometimes are more abundant than the analytes [29,30], as well as from non-targeted coexisting anthropogenic compounds or between the analytes [31]. GC/ECNI-qMS with monitoring of the characteristic ions provided more structural information and thus higher selectivity regardless of the lower sensitivity compared with the GC/ECNI-qMS, with monitoring of the base peak ions. However, the lost sensitivity could be compensated for through the introduction of a larger volume of samples into the analyzing system.

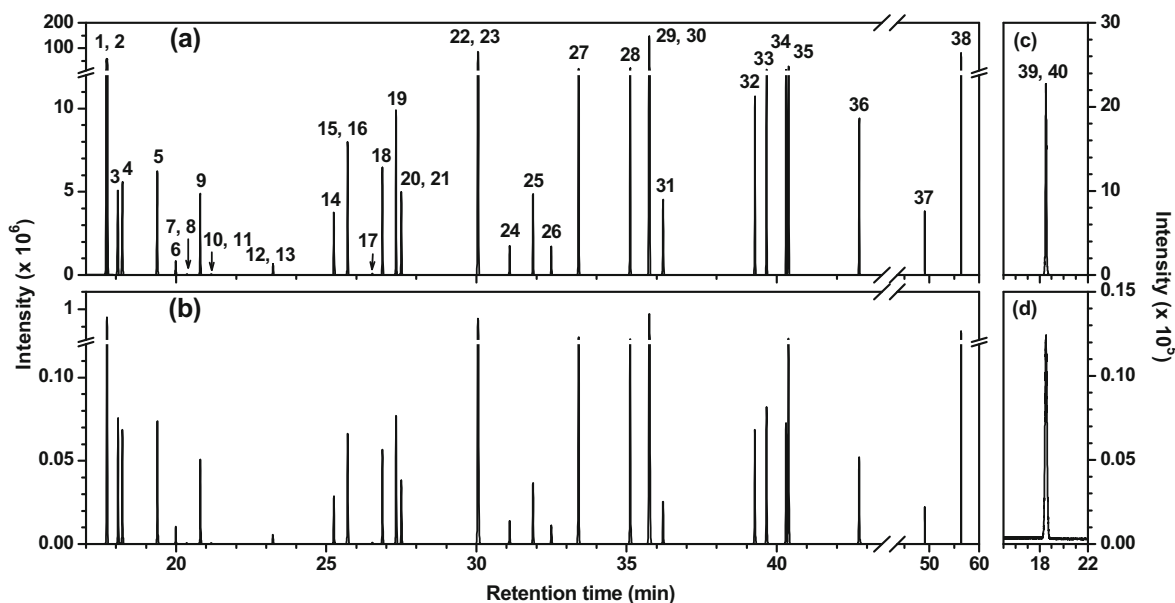
#### pLVI-GC/ECNI-qMS

The pLVI sample introduction efficiency and repeatability relative to the 1- $\mu$ L splitless injection are shown in Figure 3 for HCB, PCB-163, BDE-183, and BDE-209, which represent different degrees of volatility and thermal stability. Sample introduction efficiencies for 20 through 120  $\mu$ L sample volumes of all the analytes were higher than 83.1%, while further increase in the injection volume led to unsatisfactory introduction efficiencies for some low boiling point analytes such as HCB (see Figure 3a). When

introducing the sample through six pulsed injections of 20  $\mu$ L each, the sample introduction efficiencies obtained were between 92.3% to 99.6% for all the H-POPs studied (Figure 3b). Lower and larger sample volume per injection produced an evaporation loss of relatively volatile compounds and the liner flooding losses of the samples via the split vent, respectively. Different analytes had different optimal split ratio and initial temperature depending on their boiling points (Figure 3c and d), when the split ratio and initial temperature were increased from 10:1 to 300:1 and from 50 to 120  $^{\circ}$ C, respectively. Lower split ratio and initial temperature were insufficient for timely venting of all the solvent during the injection intervals and thus resulted in liner flooding losses of all the analytes, while higher split ratio and initial temperature led to losses of lower boiling point compounds. Similar phenomena have been reported previously [32]. As shown in Figure 3e and f, a final temperature of 280  $^{\circ}$ C combined with a pulsed high-pressure of 200 kPa was efficient in transferring the higher boiling point compounds; however, much higher temperature and pressure led to decomposition of BDE-209 and slight leakage of carrier gas.

#### Performance of the pLVI-GC/ECNI-qMS

Although many chromatographically co-eluting interferences have been previously reported when using a column of 5% diphenyl-95% dimethylsiloxane (typi-



**Figure 4.** Chromatograms obtained from the mixture of the H-POPs standards in hexane with SIM mode (the concentrations of HCB and  $^{13}\text{C}_6$ -HCB were  $10 \text{ pg mL}^{-1}$ , and those of the other H-POPs and the corresponding  $\text{D}_6$ - and  $^{13}\text{C}_{12}$ -internal standards were  $100 \text{ pg mL}^{-1}$ ) using  $120\text{-}\mu\text{L}$  pLVI (a) and  $1\text{-}\mu\text{L}$  splitless injection (b); those from BDE-209 and  $^{13}\text{C}_{12}$ -BDE-209 mixture ( $500 \text{ pg mL}^{-1}$ , respectively) using  $120\text{-}\mu\text{L}$  pLVI (c) and  $1\text{-}\mu\text{L}$  splitless injection (d). The peak numbers of H-POPs are the same as those in Table 3.

cally including the interferences between BDE-28 and PCB-118, BDE-47 and PCB-180, BDE-154 and PBB-153, PCB-163 and PCB-138 [9], baseline separation was achieved by using a DB-17MS column within 60 min divided into 20 retention time windows for all the H-POPs, except for the partial overlap between BDE-154 and PBB-153 (Figure 4). Interference between PBB-153 and BDE-154 was solved by monitoring their different characteristic ions at  $m/z = 627.5$  for PBB-153 and  $m/z = 561.6$  for BDE-154. By using pLVI, the sample amount finally introduced onto the column was increased by more than two orders of magnitude compared with the normal  $1\text{-}\mu\text{L}$  splitless injection.

Performance parameters of the pLVI-GC/ECNI-qMS developed are summarized in Table 3. The pLVI-GC/ECNI-qMS provided lower IDLs for the H-POPs, ranging from  $10 \text{ fg mL}^{-1}$  of HCB to  $87.5 \text{ pg mL}^{-1}$  of PCB-52. The IDLs were significantly improved by factors of 81.0 to 208 compared with those using the  $1\text{-}\mu\text{L}$  splitless injection, while improved by factors of 1.63 to 121 (except for the 0.011 to 0.87 of BDE-28, 47, 49, 66, 99, 138, and 153) compared with those using the GC/ECNI-qMS monitoring base peak ions with  $1\text{-}\mu\text{L}$  splitless injection. The method also exhibited good linearity with correlation coefficients of 0.9904 to 0.9999, satisfied repeatability of 0.1% to 2.2%, and reproducibility of 2.1% to 8.4% for the H-POPs. On the other hand, the method allowed the use of  $^{13}\text{C}$ -labeled and/or perdeuterated analogues as internal standards for reliable quantification of all the H-POPs studied, which is not possible for the HCHs, PCB-28, PCB-52, PBDEs, and PBB-153, when monitoring their corresponding base peak ions.

#### Method Validation and Comparison with Other Methods

The H-POP concentrations in the SRM 1946 were determined by using the pLVI-GC/ECNI-qMS, and the results are presented in Table 4. The determined concentrations are well in accordance with the certified and/or reported values [33,34], demonstrating good accuracy of the pLVI-GC/ECNI-qMS developed. Moreover, concentrations of the  $\beta$ -,  $\delta$ -HCH, and BDE-49, 138, 209 in the SRM 1946 were determined as  $0.98 \pm 0.07$ ,  $0.13 \pm 0.01$ ,  $1.81 \pm 0.08$ ,  $0.35 \pm 0.06$ , and  $0.93 \pm 0.12 \text{ ng g}^{-1}$  wet weight for the first time. Most of the H-POPs were not detected in the method blank samples except for  $\gamma$ -HCH ( $8.6 \text{ pg g}^{-1}$ ), PCB-138 ( $2.6 \text{ pg g}^{-1}$ ), PCB-153 ( $2.2 \text{ pg g}^{-1}$ ), BDE-99 ( $2.3 \text{ pg g}^{-1}$ ), BDE-100 ( $1.2 \text{ pg g}^{-1}$ ), BDE-183 ( $0.4 \text{ pg g}^{-1}$ ), and BDE-209 ( $1.21 \text{ ng g}^{-1}$ ). All the method blanks, with the exception of BDE-209, were below 1% of the concentrations determined in the SRM sample, and the blank-corrected result was reported for BDE-209. Recoveries of the internal standards from the SRM samples were 74.2% to 97.9%, and the precision of the 10 replicate measurements was less than 18.4%. MDLs of the pLVI-GC/ECNI-qMS for the H-POPs were 0.01 to  $63 \text{ pg g}^{-1}$ , most of which were lower than those listed by US EPA in Method 1668 and 1614 using the GC/HR-MS [35,36].

#### Application to Soil, Sediment, and Fish Reference Materials

The developed pLVI-GC/ECNI-qMS was applied to determine the H-POPs contents in the five CIL reference



**Table 3.** Performance of the pLVI-GC/ECNI-qMS with monitoring characteristic ions

Retention time window (min)	Retention time (min)	Compound		Instrumental detection limit (IDL, pg mL <sup>-1</sup> )	IDL's improvement factor		Linearity (r <sup>2</sup> )	Repeatability (RSD %, n = 11)	Reproducibility (RSD%, n = 7)
		Peak no.	Name		a	b			
16.0-17.9	17.698	1	<sup>13</sup> C <sub>6</sub> -HCB	0.01	81	81	0.9999	1.5	6.2
	17.700	2	HCB						
17.9-18.8	18.070	3	D <sub>6</sub> -α-HCH	0.29	100	16	0.9997	0.4	3.1
	18.215	4	α-HCH						
18.8-20.2	19.380	5	β-HCH	0.27	105	29.4	0.9996	1.0	4.8
	19.990	6	γ-HCH						
20.2-20.6	20.358	7	<sup>13</sup> C <sub>12</sub> -PCB-28	71.3	103	1.63	0.9991	1.1	5.2
	20.360	8	PCB-28						
20.6-21.0	20.810	9	δ-HCH	0.38	102	15.1	0.9999	0.7	3.9
21.0-22.2	21.178	10	<sup>13</sup> C <sub>12</sub> -PCB-52	87.5	104	2.71	0.9979	0.9	4.7
	21.180	11	PCB-52						
22.2-24.1	23.223	12	<sup>13</sup> C <sub>12</sub> -PCB-101	7.61	105	20.5	0.9981	1.4	5.9
	23.225	13	PCB-101						
24.1-25.5	25.255	14	PCB-118	0.79	106	106	0.9996	2.2	8.4
25.5-26.1	25.713	15	<sup>13</sup> C <sub>12</sub> -PCB-153	0.54	108	108	0.9997	1.0	4.9
	25.715	16	PCB-153						
26.1-27.1	26.540	17	BDE-28	33.4	108	0.011	0.9995	1.8	7.2
	26.875	18	PCB-105						
27.1-28.7	27.325	19	PCB-163	0.16	108	108	0.9997	1.7	6.9
	27.503	20	<sup>13</sup> C <sub>12</sub> -PCB-138						
28.7-30.6	27.505	21	PCB-138	1.07	107	107	0.9997	1.3	5.7
	30.053	22	<sup>13</sup> C <sub>12</sub> -PCB-180						
30.6-33.0	30.055	23	PCB-180	0.05	111	111	0.9999	0.8	4.4
	31.105	24	BDE-49						
31.8-33.0	31.880	25	BDE-47	1.58	113	0.87	0.9993	1.1	5.2
	32.490	26	BDE-66						
33.0-34.3	33.405	27	<sup>13</sup> C <sub>12</sub> -BDE-77	0.67	113	0.55	0.9999	1.8	7.1
34.3-35.4	35.120	28	BDE-100	2.14	114	0.18	0.9985	2.1	8.2
35.4-38.0	33.405	27	<sup>13</sup> C <sub>12</sub> -BDE-77	0.14	112	2.57	0.9999	1.9	7.4
	35.758	29	<sup>13</sup> C <sub>12</sub> -PCB-209						
38.0-40.0	35.760	30	PCB-209	0.02	113	113	0.9999	0.2	2.3
	36.215	31	BDE-99						
39.2-40.0	36.215	31	BDE-99	0.76	114	0.49	0.9987	1.2	5.4
	39.270	32	<sup>13</sup> C <sub>12</sub> -BDE-126						
40.0-41.6	39.660	33	BDE-85	0.25	114	1.76	0.9991	0.6	3.7
	40.280	34	PBB-153						
41.6-52.0	40.400	35	BDE-154	0.27	110	60.4	0.9994	0.4	3.2
	42.745	36	BDE-153						
49.1-52.0	49.115	37	BDE-138	0.11	110	3.09	0.9997	0.1	2.1
	52.0-60.0	56.395	38						
Short column <sup>c</sup> 16-25.0	42.745	36	BDE-153	0.38	127	0.84	0.9990	0.2	2.4
	21.740	39	<sup>13</sup> C <sub>12</sub> -BDE-209						
	21.742	40	BDE-209	0.92	113	0.59	0.9993	0.07	2.1
				0.05	131	14.4	0.9927	0.5	3.3
				3.03	208	121	0.9904	1.9	7.5

<sup>a</sup>Calculated as the ratio of the IDL of the GC/ECNI-qMS with monitoring characteristic ions using 1-μL splitless injection to that using 120-μL pLVI.

<sup>b</sup>Calculated as the ratio of the IDL of the GC/ECNI-qMS with monitoring base peak ions using 1-μL splitless injection to that of the GC/ECNI-qMS with monitoring characteristic ions using 120-μL pLVI.

<sup>c</sup>For analyzing BDE-209.

materials for an interlaboratory study from May to August 2006, and all the results are summarized in Table 5. RSDs between the five replicates for all the H-POPs determined were respectively 6.2% to 23%, 3.2% to 15%, 4.8% to 18%, 5.5% to 23%, 0.41% to 16% for the clean soil, heavily contaminated sediment, clean fish, contaminated fish, and fortified fish; and recoveries of the internal standards were 64% to 95%, 74% to 105%, 61% to 95%, 71% to 93%, and 65% to 101%, respectively. Difference in the recoveries between different reference samples might

be attributed to the difference in the matrices, especially for the different fish species due to different lipid contents.

## Conclusions

A novel pLVI-GC/ECNI-qMS with monitoring of characteristic ions was developed, validated, and applied for the simultaneous determination of typical H-POPs in environmental and biological reference materials. It could be a superior alternative, demonstrating compa-

**Table 4.** The H-POP concentrations in the standard reference material 1946 (NIST) determined using the pLVI-GC/ECNI-qMS compared with the values certified or reported, the internal standard recoveries, and the method determination limit (MDL) compared with those of the GC/HR-MS

H-POP	Concentration (ng g <sup>-1</sup> wet weight)				Recovery% (mean ± SD, n = 10)	pLVI-GC/ECNI-qMS	MDL <sup>a</sup> (pg g <sup>-1</sup> )
	Certified	Reported		Determined (mean ± SD, n = 10)			
		Ref. [33]	Ref. [34]				
<sup>13</sup> C <sub>6</sub> -HCB							
HCB	7.25 ± 0.83			7.32 ± 0.62	83.2 ± 6.8	0.01	
D <sub>6</sub> -α-HCH							
α-HCH	5.72 ± 0.65			5.67 ± 0.42	78.7 ± 5.9	0.2	
β-HCH				0.98 ± 0.07		0.2	
γ-HCH	1.14 ± 0.18			1.18 ± 0.07	85.1 ± 4.8	4.4	
<sup>13</sup> C <sub>12</sub> -PCB-28							19
PCB-28	2.00 ± 0.24			1.88 ± 0.21		44	
δ-HCH				0.13 ± 0.01		0.2	
<sup>13</sup> C <sub>12</sub> -PCB-52							
PCB-52				8.08 ± 0.9	88.9 ± 5.7	55	19
<sup>13</sup> C <sub>12</sub> -PCB-101							
PCB-101	34.6 ± 2.6			34.2 ± 3.3	88.0 ± 5.1	4.4	24
PCB-118	52.1 ± 1.0			49.6 ± 3.9		0.5	19
<sup>13</sup> C <sub>12</sub> -PCB-153							
PCB-153	170 ± 9			175 ± 10	90.9 ± 5.2	1.4	13
BDE-28		0.8 ± 0.2		0.76 ± 0.13		21	2
PCB-105	19.9 ± 0.9			18.8 ± 0.6		0.3	11
PCB-163	31.8 ± 0.8			27.8 ± 1.2		0.1	21
<sup>13</sup> C <sub>12</sub> -PCB-138							
PCB-138	115 ± 13			115 ± 11	92.2 ± 6.6	1.5	21
<sup>13</sup> C <sub>12</sub> -PCB-180							
PCB-180	74.4 ± 4.0			79.9 ± 3.0	94.9 ± 5.5	0.03	14
BDE-49				1.81 ± 0.08		0.9	3
BDE-47		31 ( 2.9		33.5 ± 0.6		3.6	2.5
BDE-66				1.62 ± 0.13		1.2	2
<sup>13</sup> C <sub>12</sub> -BDE-77							
BDE-100				9.39 ± 0.89	93.6 ± 6.1	0.9	2
<sup>13</sup> C <sub>12</sub> -PCB-209							
PCB-209	1.30 ( 0.21			1.31 ± 0.11	97.9 ± 4.7	0.01	15
BDE-99		19.4 ± 1.8		22.3 ± 1.4		1.2	4
<sup>13</sup> C <sub>12</sub> -BDE-126							
BDE-85				0.48 ± 0.10	96.8 ± 5.9	0.2	4
PBB-153				3.11 ± 0.32		0.2	
BDE-154				6.67 ± 0.73		0.1	2
BDE-153		5.1 ± 0.8		3.29 ± 0.40		0.2	2
BDE-138				0.35 ± 0.06		0.7	4
BDE-183		<0.4		0.24 ± 0.04	74.2 ± 9.4	0.2	3
<sup>13</sup> C <sub>12</sub> -BDE-209							
BDE-209				0.93 ± 0.12		63	70

<sup>a</sup>Calculated as the average method blank value plus 10 times SD based on 10 g fish tissue of wet weight.

**Table 5.** The H-POPs concentrations measured in the five reference materials (mean  $\pm$  SD,  $n = 5$ )

Compound	EDF-5183	EDF-5184	EDF-2524	EDF-2525	EDF-2526
	Concentration (ng g <sup>-1</sup> )				
HCB	2.46 $\pm$ 0.21	8.77 $\pm$ 0.53	0.41 $\pm$ 0.03	13.6 $\pm$ 1.1	3.50 $\pm$ 0.11
$\alpha$ -HCH	5.18 $\pm$ 0.32	5.57 $\pm$ 0.67	0.30 $\pm$ 0.03	2.14 $\pm$ 0.30	2.99 $\pm$ 0.17
$\beta$ -HCH	0.63 $\pm$ 0.08	4.50 $\pm$ 0.68	0.24 $\pm$ 0.02	0.86 $\pm$ 0.09	1.43 $\pm$ 0.07
$\gamma$ -HCH	1.35 $\pm$ 0.10	39.4 $\pm$ 4.3	0.21 $\pm$ 0.01	0.49 $\pm$ 0.06	26.8 $\pm$ 0.11
$\delta$ -HCH	7.58 $\pm$ 0.93	6.03 $\pm$ 0.59	0.17 $\pm$ 0.01	2.59 $\pm$ 0.20	6.76 $\pm$ 0.34
PCB-28	0.52 $\pm$ 0.08	61.2 $\pm$ 3.1	0.40 $\pm$ 0.07	8.28 $\pm$ 0.89	0.44 $\pm$ 0.04
PCB-52	1.50 $\pm$ 0.11	1470 $\pm$ 160	0.75 $\pm$ 0.09	26.7 $\pm$ 2.6	0.46 $\pm$ 0.06
PCB-101	4.89 $\pm$ 1.11	3110 $\pm$ 100	1.11 $\pm$ 0.11	82.2 $\pm$ 7.4	0.71 $\pm$ 0.10
PCB-105	0.65 $\pm$ 0.06	917 $\pm$ 101	0.29 $\pm$ 0.03	37.6 $\pm$ 4.3	0.12 $\pm$ 0.01
PCB-118	6.39 $\pm$ 0.41	2560 $\pm$ 260	0.70 $\pm$ 0.05	129 $\pm$ 10	0.32 $\pm$ 0.04
PCB-138	2.03 $\pm$ 0.30	3460 $\pm$ 290	1.03 $\pm$ 0.15	196 $\pm$ 15	0.43 $\pm$ 0.07
PCB-153	2.26 $\pm$ 0.34	4010 $\pm$ 500	1.49 $\pm$ 0.11	275 $\pm$ 17	0.61 $\pm$ 0.09
PCB-163	0.36 $\pm$ 0.08	844 $\pm$ 91	0.82 $\pm$ 0.10	40.3 $\pm$ 4.6	0.35 $\pm$ 0.04
PCB-180	0.99 $\pm$ 0.08	2650 $\pm$ 300	0.47 $\pm$ 0.05	109 $\pm$ 7	0.14 $\pm$ 0.02
PCB-209	0.25 $\pm$ 0.03	7.79 $\pm$ 1.16	0.021 $\pm$ 0.003	3.09 $\pm$ 0.17	0.009 $\pm$ 0.001
	Concentration (pg g <sup>-1</sup> )				
PBB-153	37.8 $\pm$ 2.9	59.7 $\pm$ 5.4	66.5 $\pm$ 5.5	3100 $\pm$ 270	11.8 $\pm$ 1.0
BDE-28	29.7 $\pm$ 3.4	26.6 $\pm$ 3.0	23.7 $\pm$ 2.6	274 $\pm$ 31	16.3 $\pm$ 1.5
BDE-47	267 $\pm$ 31	99.8 $\pm$ 7.1	516 $\pm$ 62	8030 $\pm$ 450	30.5 $\pm$ 2.7
BDE-49	14.4 $\pm$ 1.3	139 $\pm$ 15.1	121 $\pm$ 9.8	413 $\pm$ 29	12.1 $\pm$ 1.0
BDE-66	20.6 $\pm$ 2.5	62.1 $\pm$ 6.9	25.9 $\pm$ 2.4	568 $\pm$ 76	2.6 $\pm$ 0.3
BDE-85	22.3 $\pm$ 2.8	24.5 $\pm$ 1.9	23.7 $\pm$ 2.6	375 $\pm$ 57	5.1 $\pm$ 0.5
BDE-99	32.5 $\pm$ 4.2	50.5 $\pm$ 3.4	44.9 $\pm$ 4.8	1690 $\pm$ 150	9.8 $\pm$ 1.0
BDE-100	12.7 $\pm$ 1.6	24.4 $\pm$ 1.3	35.9 $\pm$ 4.0	1440 $\pm$ 120	9.6 $\pm$ 0.9
BDE-138	12.6 $\pm$ 1.3	12.8 $\pm$ 1.4	22.1 $\pm$ 3.9	378 $\pm$ 86	7.1 $\pm$ 0.7
BDE-153	34.1 $\pm$ 2.5	10.9 $\pm$ 1.2	15.4 $\pm$ 1.3	2010 $\pm$ 200	3.3 $\pm$ 0.3
BDE-154	27.2 $\pm$ 1.9	26.0 $\pm$ 1.8	12.2 $\pm$ 1.6	2110 $\pm$ 200	nd
BDE-183	223 $\pm$ 32	81.0 $\pm$ 8.9	40.9 $\pm$ 2.4	156 $\pm$ 25	19.1 $\pm$ 1.3
BDE-209	691 $\pm$ 63	7620 $\pm$ 860			

nd, not detected.

rable selectivity and lower detection limit, to GC/HR-MS. Using <sup>13</sup>C-labeled and/or perdeuterated internal standard calibration for reliable quantification was an additional feature of this method. Furthermore, the method could be extended to the determination of other trace H-POPs in various environmental and biological matrices at pg g<sup>-1</sup> level or below, in combination with suitable matrix-selective extraction and analyte-specific cleanup procedures soon.

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## References

- Eljarrat, E.; Barcelo, D. Priority Lists for Persistent Organic Pollutants and Emerging Contaminants Based on Their Relative Toxic Potency in Environmental Samples. *Trends Anal. Chem.* **2003**, *22*, 655–665.
- Koester, C. J.; Simonich, S. L.; Esser, B. K. Environmental Analysis. *Anal. Chem.* **2003**, *75*, 2813–2829.
- Liu, H. X.; Zhang, Q. H.; Cai, Z. W.; Li, A.; Wang, Y. W.; Jiang, G. B. Separation of Polybrominated Diphenyl Ethers, Polychlorinated Biphenyls, Polychlorinated Dibenzo-p-Dioxins, and Dibenzo-Furans in Environmental Samples Using Silica Gel and Florisil Fractionation Chromatography. *Anal. Chim. Acta.* **2006**, *557*, 314–320.
- Pirard, C.; De Pauw, E.; Focant, J.-F. New Strategy for Comprehensive Analysis of Polybrominated Diphenyl Ethers, Polychlorinated Dibenzo-p-Dioxins, Polychlorinated Dibenzofurans, and Polychlorinated Biphenyls by Gas Chromatography Coupled with Mass Spectrometry. *J. Chromatogr. A* **2003**, *998*, 169–181.
- Hites, R. A. Polybrominated Diphenyl Ethers in the Environment and in People: A Meta-Analysis of Concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945–956.
- Santos, F. J.; Galceran, M. T. The Application of Gas Chromatography to Environmental Analysis. *Trends Anal. Chem.* **2002**, *21*, 672–685.
- de Boer, J. Capillary Gas Chromatography for the Determination of Halogenated Microcontaminants. *J. Chromatogr. A* **1999**, *843*, 179–198.
- Chu, S. G.; Hong, C.-S.; Rattner, B. A.; McGowan, P. C. Methodological Refinements in the Determination of 146 Polychlorinated Biphenyls, Including Nonortho- and Monoortho-Substituted PCBs, and 26 organochlorine pesticides as Demonstrated in Heron Eggs. *Anal. Chem.* **2003**, *75*, 1058–1066.
- Alaee, M.; Backus, S.; Cannon, C. Potential Interference of PBDEs in the Determination of PCBs and Other Organochlorine Contaminants Using Electron Capture Detection. *J. Sep. Sci.* **2001**, *24*, 465–469.
- Korytar, P.; Haglund, P.; de Boer, J.; Brinkman, U. A. T. Comprehensive Two-Dimensional Gas Chromatography for the Analysis of Organohalogenated Microcontaminants. *Trends Anal. Chem.* **2006**, *25*, 373–396.
- Liu, H. X.; Zhang, Q. H.; Song, M. Y.; Jiang, G. B.; Cai, Z. W. Method of Development for the Analysis of Polybrominated Diphenyl Ethers, Polychlorinated Biphenyls, Polychlorinated Dibenzo-p-Dioxins, and Dibenzo-Furans in Single Extract of Sediment Samples. *Talanta* **2006**, *70*, 20–25.
- Zeng, E. Y.; Chou, C. C.; Yu, C. Potential Application of Gas Chromatography/Tandem Mass Spectrometry in the Measurement of Coeluting Isomers. *Anal. Chem.* **2002**, *74*, 4513–4518.
- Clarkson, P. J.; Larrabal-Moya, D.; Staton, I.; McLeod, C. W.; Ward, D. B.; Sharifi, V. N.; Swithenbank, J. The Use of Tree Bark as a Passive Sampler for Polychlorinated Dibenzo-p-Dioxins and Furans. *Int. J. Environ. Anal. Chem.* **2002**, *82*, 843–850.
- Cai, Z. W.; Jiang, G. B. Determination of Polybrominated Diphenyl Ethers in Soil from e-Waste Recycling Site. *Talanta* **2006**, *70*, 88–90.
- Hernandez, F.; Portoles, T.; Pitarch, E.; Lopez, F. J.; Beltran, J.; Vazquez, C. Potential of Gas Chromatography Coupled to Triple Quadrupole Mass Spectrometry for Quantification and Confirmation of Organohalo-

- gen Xenoestrogen Compounds in Human Breast Tissues. *Anal. Chem.* **2005**, *77*, 7662–7672.
16. Focant, J.-F.; Sjödin, A.; Turner, W. E.; Patterson, D. G., Jr. Measurement of Selected Polybrominated Diphenyl Ethers, Polybrominated and Polychlorinated Biphenyls, and Organochlorine Pesticides in Human Serum and Milk Using Comprehensive Two-Dimensional Gas Chromatography Isotope Dilution Time-of-Flight Mass Spectrometry. *Anal. Chem.* **2004**, *76*, 6313–6320.
  17. Korytar, P.; Parera, J.; Leonards, P. E. G.; de Boer, J.; Brinkman, U. A. T. Quadrupole Mass Spectrometer Operating in the Electron-Capture Negative Ion Mode as Detector for Comprehensive Two-Dimensional Gas Chromatography. *J. Chromatogr. A* **2005**, *1067*, 255–264.
  18. Santos, F. J.; Galceran, M. T. Modern Developments in Gas Chromatography-Mass Spectrometry-Based Environmental Analysis. *J. Chromatogr. A* **2003**, *1000*, 125–151.
  19. Rothweiler, B.; Berset, J.-D. High Sensitivity of Ortho-Substituted Polychlorobiphenyls in Negative Ion Mass Spectrometry (NCI-MS): A Comparison with EI-MS and ECD for the Determination of Regulatory PCBs in Soils. *Chemosphere* **1999**, *38*, 1517–1532.
  20. Hyötyläinen, T.; Hartonen, K. Determination of Brominated Flame Retardants in Environmental Samples. *Trends Anal. Chem.* **2002**, *21*, 13–29.
  21. Stapleton, H. M. Instrumental Methods and Challenges in Quantifying Polybrominated Diphenyl Ethers in Environmental Extracts: A review. *Anal. Bioanal. Chem.* **2006**, *386*, 807–817.
  22. Eljarrat, E.; Lacorte, S.; Barcelo, D. Optimization of Congener-Specific Analysis of 40 Polybrominated Diphenyl Ethers by gas Chromatography/Mass Spectrometry. *J. Mass Spectrom.* **2002**, *37*, 76–84.
  23. Covaci, A.; de Boer, J.; Ryan, J. J.; Voorspoels, S.; Schepens, P. Determination of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls in Human Adipose Tissue by Large-Volume Injection Narrow-Bore Capillary Gas Chromatography/Electron Impact Low-Resolution Mass Spectrometry. *Anal. Chem.* **2002**, *74*, 790–798.
  24. Ackerman, L. K.; Wilson, G. R.; Simonich, S. L. Quantitative Analysis of 39 Polybrominated Diphenyl Ethers by Isotope Dilution GC/Low-Resolution MS. *Anal. Chem.* **2005**, *77*, 1979–1987.
  25. Bjorklund, J.; Tollback, P.; Hiarné, C.; Dyremark, E.; Ostman, C. Influence of the Injection Technique and the Column System on Gas Chromatographic Determination of Polybrominated Diphenyl Ethers. *J. Chromatogr. A* **2004**, *1041*, 201–210.
  26. Bjorklund, J.; Tollback, P.; Ostman, C. Mass Spectrometric Characteristics of Decabromodiphenyl Ether and the Application of Isotopic Dilution in the Electron Capture Negative Ionization Mode for the Analysis of Polybrominated Diphenyl ethers. *J. Mass Spectrom.* **2003**, *38*, 394–400.
  27. Ong, V. S.; Hites, R. A. Electron Capture Mass Spectrometry of Organic Environmental Contaminants. *Mass Spectrom. Rev.* **1994**, *13*, 259–283.
  28. Zeng, X.; Freeman, P. K.; Vasil'ev, Y. V.; Voinov, V. G.; Simonich, S. L.; Barofsky, D. F. Theoretical Calculation of Thermodynamic Properties of Polybrominated Diphenyl Ethers. *J. Chem. Eng. Data* **2005**, *50*, 1548–1556.
  29. Vetter, W. A GC/ECNI-MS Method for the Identification of Lipophilic Anthropogenic and Natural Brominated Compounds in Marine Samples. *Anal. Chem.* **2001**, *73*, 4951–4957.
  30. Teuten, E. L.; Xu, L.; Reddy, C. M. Two Abundant Bioaccumulated Halogenated Compounds are Natural Products. *Science* **2005**, *307*, 917–920.
  31. Eljarrat, E.; de la Cal, A.; Barcelo, D. Potential Chlorinated and Brominated Interferences on the Polybrominated Diphenyl Ether Determinations by Gas Chromatography-Mass Spectrometry. *J. Chromatogr. A* **2003**, *1008*, 181–192.
  32. Tollback, P.; Bjorklund, J.; Ostman, C. Large-Volume Programmed-Temperature Vaporizer Injection for Fast Gas Chromatography with Electron Capture and Mass Spectrometric Detection of Polybrominated Diphenyl Ethers. *J. Chromatogr. A* **2003**, *991*, 241–253.
  33. Stapleton, H.; Schantz, M.; Wise, S. Measurement of Polybrominated Diphenyl Ethers in Environmental Matrix Standard Reference Materials. *Organohalogen Comp.* **2004**, *66*, 3745–3748.
  34. Zhu, L. Y.; Hites, R. A. Determination of Polybrominated Diphenyl Ethers in Environmental Standard Reference Materials. *Anal. Chem.* **2003**, *75*, 6696–6700.
  35. US EPA Method 1668 Revision A, Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS.
  36. US EPA Draft Method 1614, Brominated Diphenyl Ethers in Water, Soil, Sediment, and Tissue by HRGC/HRMS.