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}C-labeled and perdeuterated analogues as internal standards for reliable quantification. pLVI up to 120 μL improved the instrumental detection limits down to pg–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 = 0.9904–0.9999) within 0.5 to 50,000 pg mL^{-1} for PCBs and 0.05 to 5000 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 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

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), polychlorinated 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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1044-0305/07/$32.00
doi:10.1016/j.jasms.2007.04.019

Published online April 29, 2007
Received February 28, 2007
Revised April 20, 2007
Accepted April 22, 2007

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}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 μL achieving selective determination at the low 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 (Br_{7-10}) PBDEs remained insufficient. Using ECNI, Ackerman et al. [24] novelly monitored specific large mass-to-charge ratio (m/z) fragment ions ($[M - H_x\text{-}Br_y]^-$) instead of the conventional bromine ion ($^{78.9/80.9}[Br]^-$), performing isotope dilution quantification of 39 PBDEs with low 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}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 (α, β, γ, δ-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}C-labeled and/or perdeuterated analogues used as internal standards are listed in Table 1. All native and ^{13}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 D_6-α-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 (H_2SO_4, Sinic Chemical Reagent Company, SCRC) was of analytical reagent (AR) grade. Before use, anhydrous sodium sulfate (Na_2SO_4, AR, SCRC) and neutral alumina (100–200 mesh, SCRC) were extracted with dichloromethane and baked at 350 °C for 3 h and 600 °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 × 0.25 mm i.d. × 0.25 μm 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 × 0.25 mm i.d. × 0.25 μm film thickness (J & W Scientific) to reduce possible thermal degradation [25]. A deactivated guard column of 5 m length × 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-μL injection and the latter for pLVI. For the splitless injection, the injector temperature was held at 280 °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 μL, 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/EI-qMS			GC/CI-qMS			GC/ECNI-gMS					
								Monitoring base peak ions			Monitoring characteristic ions		
Name	IUPAC no. or abbr.	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
Organochlorine pesticide (OCP)													
$^{13}C_6$-Hexachlorobenzene	$^{13}C_6$-HCB	289.8	291.8, 287.8		290.8	292.8, 288.8		289.8	291.8, 287.8		289.8	291.8, 287.8	
Hexachlorobenzene	HCB	283.8	285.8, 281.8	52.5	284.8	286.8, 282.8	792	283.8	285.8, 281.8	0.81	283.8	285.8, 281.8	0.81
Hexachlorocyclohexane (HCH) isomer													
	D_6-α-HCH	224.8	222.8, 186.9		224.8	222.8, 186.9		71.0	73.0, 35.0		260.9	258.9, 262.9	
	α-HCH	218.8	216.8, 180.9	292	218.8	216.8, 180.9	2090	71.0	73.0, 35.0	4.63	254.9	252.9, 256.9	29.1
	β-HCH	218.8	216.8, 180.9	364	218.8	216.8, 180.9	1920	71.0	73.0, 35.0	7.95	254.9	252.9, 256.9	28.4
	γ-HCH	218.8	216.8, 180.9	323	218.8	216.8, 180.9	1470	71.0	73.0, 35.0	16.7	254.9	252.9, 256.9	193
	δ-HCH	218.8	216.8, 180.9	367	218.8	216.8, 180.9	2350	71.0	73.0, 35.0	5.72	254.9	252.9, 256.9	38.6
Polychlorinated biphenyl (PCB) congener													
$^{13}C_{12}$-2,4,4′-TrCB	$^{13}C_{12}$-PCB-28	268.0	270.0, 198.0		268.9	270.9, 272.9		35.0	37.0		267.9	269.9, 271.9	
2,4,4′-TrCB	PCB-28	255.9	257.9, 186.0	117	256.9	258.9, 260.9	887	35.0	37.0	116	255.9	257.9, 259.9	7310
$^{13}C_{12}$-2,2′,5,5′-TeCB	$^{13}C_{12}$-PCB-52	303.9	301.9, 231.9		304.9	302.9, 306.9		35.0	37.0		303.9	301.9, 305.9	
2,2′,5,5′-TeCB	PCB-52	291.9	289.9, 219.9	162	292.9	290.9, 294.9	929	35.0	37.0	237	291.9	289.9, 293.9	9110
$^{13}C_{12}$-2,2′,4,5,5′-PeCB	$^{13}C_{12}$-PCB-101	337.9	339.9, 265.9		338.9	340.9, 336.9		35.0	37.0		337.9	339.9, 335.9	
2,2′,4,5,5′-PeCB	PCB-101	325.9	327.9, 253.9	176	326.9	328.9, 324.9	762	35.0	37.0	156	325.9	327.9, 323.9	802
2,3,3′,4,4′-PeCB	PCB-105	325.9	327.9, 253.9	140	326.9	328.9, 324.9	852	325.9	327.9, 323.9	45.5	325.9	327.9, 323.9	45.5
2,3′,4,4′,5-PeCB	PCB-118	325.9	327.9, 253.9	138	326.9	328.9, 324.9	806	325.9	327.9, 323.9	83.5	325.9	327.9, 323.9	83.5
$^{13}C_{12}$-2,2′,3,4,4′,5′-HxCB	$^{13}C_{12}$-PCB-138	371.8	373.8, 301.9		372.8	374.8, 370.8		371.9	373.9, 369.9		371.9	373.9, 369.9	
2,2′,3,4,4′,5′-HxCB	PCB-138	359.8	361.8, 289.9	214	360.8	362.8, 358.8	782	359.8	361.8, 357.8	115	359.8	361.8, 357.8	115
$^{13}C_{12}$-2,2′,4,4′5,5′-HxCB	$^{13}C_{12}$-PCB-153	371.8	373.8, 301.9		372.8	374.8, 370.8		371.9	373.9, 369.9		371.9	373.9, 369.9	
2,2′,4,4′5,5′-HxCB	PCB-153	359.8	361.8, 289.9	193	360.8	362.8, 358.8	768	359.8	361.8, 357.8	58.5	359.8	361.8, 357.8	58.5
2,3,3′,4′,5,6-HxCB	PCB-163	359.8	361.8, 289.9	202	360.8	362.8, 358.8	774	359.8	361.8, 357.8	17.2	359.8	361.8, 357.8	17.2
$^{13}C_{12}$-2,2′,3,4,4′,5,5′-HpCB	$^{13}C_{12}$-PCB-180	405.8	407.8, 335.9		406.8	408.8, 410.8		405.8	407.8, 409.8		405.8	407.8, 409.8	
2,2′,3,4,4′,5,5′-HpCB	PCB-180	393.8	395.8, 323.9	197	394.8	396.8, 398.8	1170	393.8	395.8, 397.8	5.55	393.8	395.8, 397.8	5.55
$^{13}C_{12}$-2,2′,3,3′,4,4′,5,5′,6,6′-DeCB	$^{13}C_{12}$-PCB-209	509.7	511.7, 507.7		509.7	511.7, 507.7		509.7	511.7, 507.7		509.7	511.7, 507.7	
2,2′,3,3′,4,4′,5,5′,6,6′-DeCB	PCB-209	497.6	499.6, 495.6	381	498.6	500.6, 496.6	1830	497.7	499.7, 495.7	2.25	497.7	499.7, 495.7	2.25
Polybrominated biphenyl (PBB) congener													
2,2′,4,4′,5,5′-HxBB	PBB-153	627.5	629.5, 546.6	89.5	628.5	630.5, 547.6	1220	80.9	78.9	16.3	627.5	629.5, 625.5	29.8
Polybrominated diphenyl ether (PBDE) congener													
2,4,4′-TrBDE	BDE-28	405.8	407.8, 247.0	77.6	406.8	408.8, 500.8	493	80.9	78.9, 160.8	0.38	325.9	323.9, 247.9	3620
2,2′,4,4′-TeBDE	BDE-47	485.7	483.7, 325.9	90.5	486.7	484.7, 488.7	897	80.9	78.9, 160.8	0.37	403.8	405.8, 325.9	75.6
2,2′,4,5′-TeBDE	BDE-49	485.7	483.7, 325.9	438	486.7	484.7, 488.7	2520	80.9	78.9, 160.8	1.37	403.8	405.8, 325.9	178
2,3′,4,4′-TeBDE	BDE-66	485.7	483.7, 325.9	146	486.7	484.7, 488.7	983	80.9	78.9, 160.8	0.38	403.8	405.8, 325.9	244
$^{13}C_{12}$-3,3′,4,4′-TeBDE	$^{13}C_{12}$-BDE-77	497.7	495.7, 499.7		498.7	496.7, 500.7		80.9	78.9, 160.8		497.7	495.7, 499.7	
2,2′,3,4,4′-PeBDE	BDE-85	563.6	565.6, 403.8	275	564.6	566.6, 568.6	1030	80.9	78.9, 160.8	0.44	483.7	485.7, 328.8	28.4
2,2′,4,4′,5-PeBDE	BDE-99	563.6	565.6, 403.8	139	564.6	566.6, 568.6	1310	80.9	78.9, 160.8	0.37	483.7	485.7, 328.8	86.6
2,2′,4,4′,6-PeBDE	BDE-100	563.6	565.6, 403.8	147	564.6	566.6, 568.6	897	80.9	78.9, 160.8	0.36	483.7	485.7, 328.8	15.7
$^{13}C^{12}$-3,3′,4,4′5-PeBDE	$^{13}C_{12}$-BDE-126	575.6	577.6, 573.6		576.6	578.6, 580.6		80.9	78.9, 160.8		575.6	577.6, 573.6	
2,2′,3,4,4′,5′-HxBDE	BDE-138	643.5	641.5, 483.6	188	644.5	642.5, 646.5	2410	80.9	78.9, 160.8	0.54	561.6	563.6, 483.7	104
2,2′,4,4′,5,5′-HxBDE	BDE-153	643.5	641.5, 483.6	145	644.5	642.5, 646.5	2210	80.9	78.9, 160.8	0.32	561.6	563.6, 483.7	48.2
2,2′,4,4′,5,6′-HxBDE	BDE-154	643.5	641.5, 483.6	116	644.5	642.5, 646.5	1610	80.9	78.9, 160.8	0.34	561.6	563.6, 483.7	12.1
2,2′,3,4,4′,5′,6-HpBDE	BDE-183	721.4	723.4, 561.6	244	722.4	724.4, 726.4	2810	80.9	78.9, 160.8	0.72	642.5	640.5, 561.6	6.56
$^{13}C_{12}$-2,2′,3,3′,4,4′,5,5′,6,6′-DeBDE	$^{13}C_{12}$-BDE-209	811.3	971.1, 973.2		972.1	970.1, 974.1		492.6	494.6, 496.6		730.4	732.4, 492.6	
2,2′,3,3′,4,4′,5,5′,6,6′-DeBDE	BDE-209	799.3	959.1, 961.2	789	960.1	958.1, 962.1	9670	486.6	488.6, 490.6	366	718.4	720.4, 486.6	631

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[a]	ECNI-qMS[b]
Electron energy (eV)	40-80	5[c], 2[d]	60[e], 70[f]	55[e], 65[f]	70[e], 60[f]	56[e], 60[f]
Filament emission current (μA)	30-70	5[c], 2[d]	55[e], 60[f]	55[e], 60[f]	65[e], 60[f]	50[e], 55[f]
Source temperature (°C)	150-260	10[c], 5[d]	200[e], 250[f]	190[e], 250[f]	250[e], 250[f]	195[e], 250[f]
Moderating gas type	CH_4, i-C_4H_{10}	-	-	i-C_4H_{10}[e,f]	i-C_4H_{10}[e,f]	i-C_4H_{10}[e,f]
Moderating gas pressure (10^{-3} Pa)	2.0-5.0	0.5[c], 0.1[d]	-	3.5[e], 2.5[f]	2.5[e], 2.0[f]	3.6[e], 3.2[f]

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

280 °C. Helium (He, 99.999%, Linde, Xiamen, China) was used as the GC carrier, and methane (CH_4, 99.995%, Linde) and isobutane (i-C_4H_{10}, 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-μL 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 comparable to the 1-μL splitless injection, and that the decomposition of thermally labile components was insignificant. As illustrated in Figure 1, 120 μL was introduced onto the column by six pulsed injections of 20 μL each at an initial temperature of 75 °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. × 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 °C for transferring the analytes

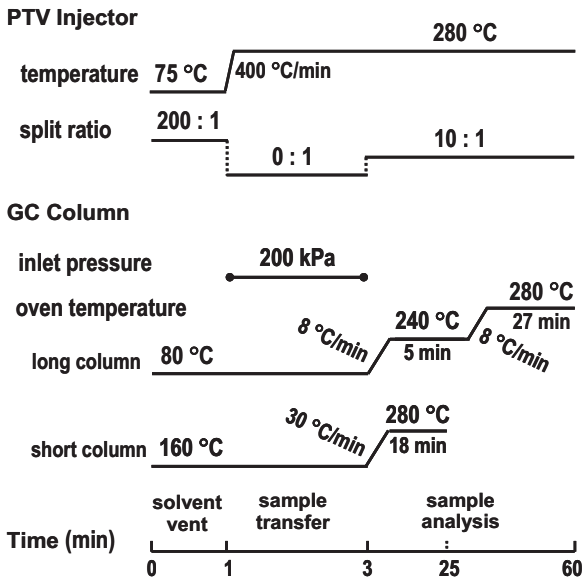

Figure 1. Parameters of the PTV temperature and split ratio as well as the GC column inlet pressure and oven temperature during solvent vent (0–1 min), sample transfer (1–3 min), sample analysis (3–25 min for BDE-209, and 3–60 min for the other all H-POPs).

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 pg mL^{-1} for the PBDEs, PBB-153, and OCPs, and 0.5, 5, 50, 500, 5000, and 50,000 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 carps 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 interferents, 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 Na_2SO_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 ~1 mL using nitrogen (N_2) stream, followed by solvent exchange into 5 mL hexane. The extract then had 5 mL concentrated H_2SO_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. × 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 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 ($[M]^+$) are the base peak ions for all the H-POPs with the exception of HCHs, which fragment ions $[M - Cl_{2,3,5}]^+$ are base peak ions. In the PCI mass spectra, protonated molecular ions ($[MH]^+$) are the base peak ions for all the HOCs except for the fragment ions $[MH - Cl_2]^+$ for HCHs. The ECNI mass spectra of HCB and highly chlorinated PCBs (containing more than four chlorine atoms) exhibited dominating molecular ions ($[M]^-$) as the base peak ions, while those of the HCHs showed strong to moderate fragment $[Cl]^-$, $[HCl_2]^-$, and $[M - HCl]^-$ ions. Nevertheless, the ECNI mass spectra of the lower chlorinated PCB-28 and 52 as well as PBB-153 and PBDEs yield predominant $[Cl]^-$ and $[Br]^-$, respectively, but weak $[M]^-$. Exceptionally, the ECNI mass spectra of BDE-209 showed intense to moderate $[C_6Br_5O]^-$, $[C_6Br_4O]^-$, and $[Br]^-$ agreeing with the findings of previous investigators [26]; besides, $[M - Br_{1-5}]^-$ due to the subsequent losses of bromine atoms from the $[M]^-$ were observed in low 1.3% to 17% abundance with the expected isotopic pattern.

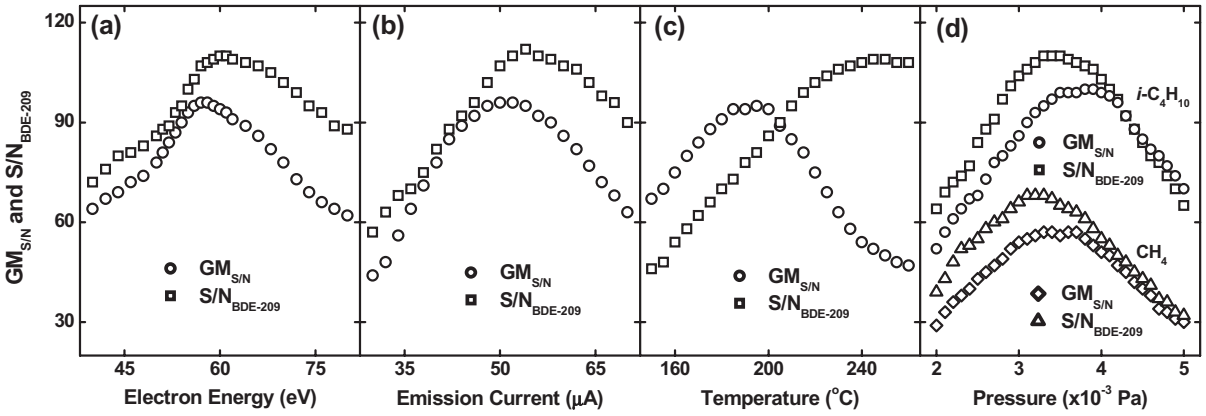

Figure 2. Geometric mean of the signal to noise ratios (S/N) for the quantitative ions (see Table 1) of all the H-POPs except BDE-209 ($GM_{S/N}$) and the S/N for the quantitative ion of BDE-209 ($S/N_{BDE\text{-}209}$) as functions of electron energy (eV) (**a**), filament emission current (μA) (**b**), ion source temperature (°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 γ-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 $PBDE_{n\ =\ 3\text{–}7}$, $[M - HCl]^-$ 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 ~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.

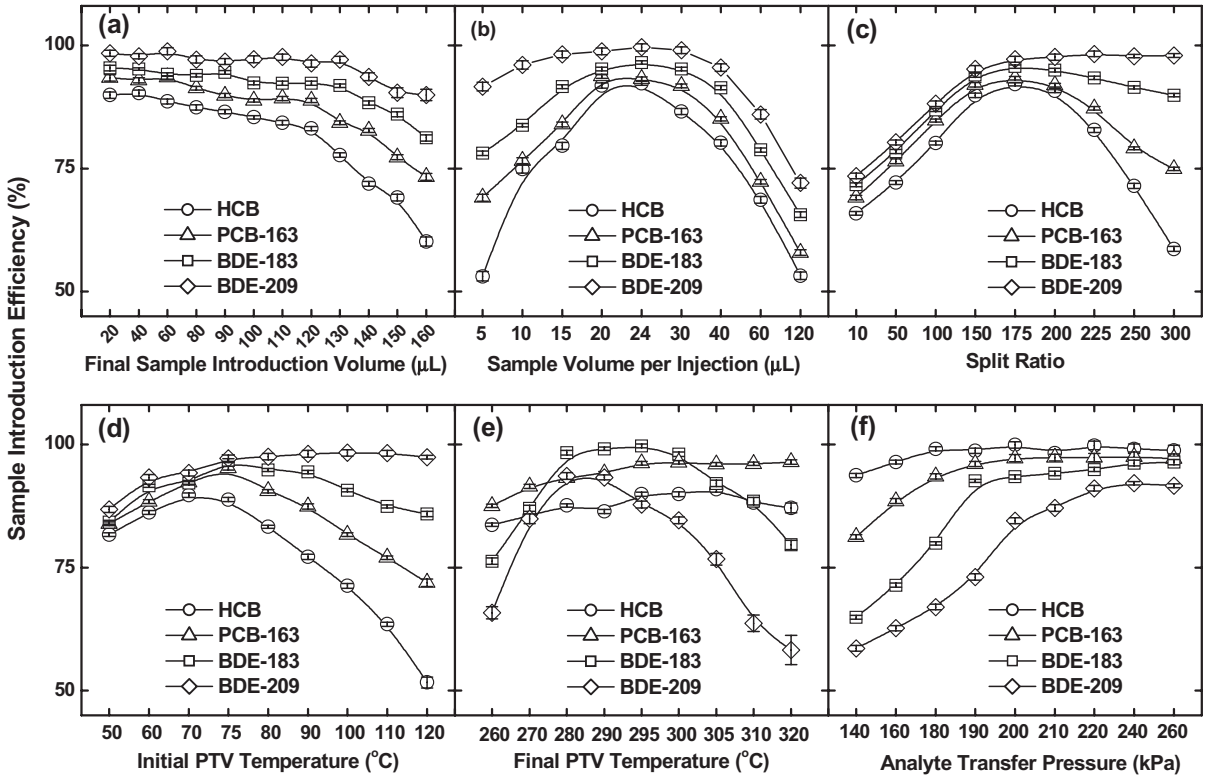

Figure 3. Sample introduction efficiency and repeatability (SD, $n = 11$, shown as error bars), of the pLVI for HCB, PCB-163, BDE-183, and BDE-209 as a function of final sample introduction volume (**a**), sample volume per injection (**b**), split ratio (**c**), initial PTV temperature (**d**), final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

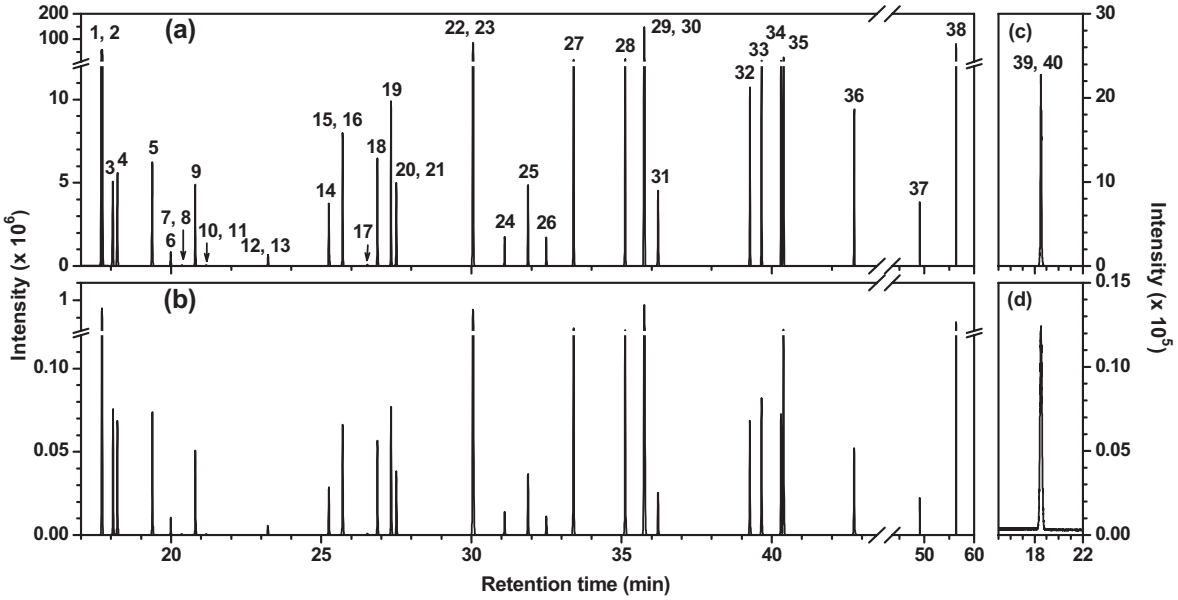

Figure 4. Chromatograms obtained from the mixture of the H-POPs standards in hexane with SIM mode (the concentrations of HCB and $^{13}C_6$-HCB were 10 pg mL^{-1}, and those of the other H-POPs and the corresponding D_6- and $^{13}C_{12}$-internal standards were 100 pg mL^{-1}) using 120-μL pLVI (**a**) and 1-μL splitless injection (**b**); those from BDE-209 and $^{13}C_{12}$-BDE-209 mixture (500 pg mL^{-1}, respectively) using 120-μL pLVI (**c**) and 1-μL 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-μL 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 fg mL^{-1} of HCB to 87.5 pg mL^{-1} of PCB-52. The IDLs were significantly improved by factors of 81.0 to 208 compared with those using the 1-μL 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-μL 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}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 β-, δ-HCH, and BDE-49, 138, 209 in the SRM 1946 were determined as 0.98 ± 0.07, 0.13 ± 0.01, 1.81 ± 0.08, 0.35 ± 0.06, and 0.93 ± 0.12 ng g^{-1} wet weight for the first time. Most of the H-POPs were not detected in the method blank samples except for γ-HCH (8.6 pg g^{-1}), PCB-138 (2.6 pg g^{-1}), PCB-153 (2.2 pg g^{-1}), BDE-99 (2.3 pg g^{-1}), BDE-100 (1.2 pg g^{-1}), BDE-183 (0.4 pg g^{-1}), and BDE-209 (1.21 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 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^{-1})	IDL's improvement factor		Linearity (r^2)	Repeatability (RSD %, n = 11)	Reproducibility (RSD%, n = 7)
		Peak no.	Name		a	b			
16.0-17.9	17.698	1	$^{13}C_6$-HCB						
	17.700	2	HCB	0.01	81	81	0.9999	1.5	6.2
17.9-18.8	18.070	3	D_6-α-HCH						
	18.215	4	α-HCH	0.29	100	16	0.9997	0.4	3.1
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	1.91	101	8.74	0.9999	1.3	5.6
20.2-20.6	20.358	7	13C12-PCB-28						
	20.360	8	PCB-28	71.3	103	1.63	0.9991	1.1	5.2
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	$^{13}C_{12}$-PCB-52						
	21.180	11	PCB-52	87.5	104	2.71	0.9979	0.9	4.7
22.2-24.1	23.223	12	$^{13}C_{12}$-PCB-101						
	23.225	13	PCB-101	7.61	105	20.5	0.9981	1.4	5.9
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	$^{13}C_{12}$-PCB-153						
	25.715	16	PCB-153	0.54	108	108	0.9997	1.0	4.9
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	0.43	106	106	0.9998	1.2	5.3
27.1-28.7	27.325	19	PCB-163	0.16	108	108	0.9997	1.7	6.9
	27.503	20	$^{13}C_{12}$-PCB-138						
	27.505	21	PCB-138	1.07	107	107	0.9997	1.3	5.7
28.7-30.6	30.053	22	$^{13}C_{12}$-PCB-180						
	30.055	23	PCB-180	0.05	111	111	0.9999	0.8	4.4
30.6-33.0	31.105	24	BDE-49	1.58	113	0.87	0.9993	1.1	5.2
	31.880	25	BDE-47	0.67	113	0.55	0.9999	1.8	7.1
	32.490	26	BDE-66	2.14	114	0.18	0.9985	2.1	8.2
33.0-34.3	33.405	27	$^{13}C_{12}$-BDE-77						
34.3-35.4	35.120	28	BDE-100	0.14	112	2.57	0.9999	1.9	7.4
35.4-38.0	35.758	29	$^{13}C_{12}$-PCB-209						
	35.760	30	PCB-209	0.02	113	113	0.9999	0.2	2.3
38.0-40.0	36.215	31	BDE-99	0.76	114	0.49	0.9987	1.2	5.4
	39.270	32	$^{13}C_{12}$-BDE-126						
	39.660	33	BDE-85	0.25	114	1.76	0.9991	0.6	3.7
40.0-41.6	40.280	34	PBB-153	0.27	110	60.4	0.9994	0.4	3.2
	40.400	35	BDE-154	0.11	110	3.09	0.9997	0.1	2.1
41.6-52.0	42.745	36	BDE-153	0.38	127	0.84	0.9990	0.2	2.4
	49.115	37	BDE-138	0.92	113	0.59	0.9993	0.07	2.1
52.0-60.0	56.395	38	BDE-183	0.05	131	14.4	0.9927	0.5	3.3
Short column[c]									
16-25.0	21.740	39	$^{13}C_{12}$-BDE-209						
	21.742	40	BDE-209	3.03	208	121	0.9904	1.9	7.5

[a]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.
[b]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.
[c]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

	Concentration (ng g^{-1} wet weight)						
		Reported				MDL[a] (pg g^{-1})	
H-POP	Certified	Ref. [33]	Ref. [34]	Determined (mean±SD, n = 10)	Recovery% (mean±SD, n = 10)	pLVI-GC/ECNI-qMS	GC/HR-MS [35, 36]
$^{13}C_6$-HCB					83.2 ± 6.8		
HCB	7.25 ± 0.83			7.32 ± 0.62		0.01	
D_6-α-HCH					78.7 ± 5.9		
α-HCH	5.72 ± 0.65			5.67 ± 0.42		0.2	
β-HCH				0.98 ± 0.07		0.2	
γ-HCH	1.14 ± 0.18			1.18 ± 0.07		4.4	
$^{13}C_{12}$-PCB-28					85.1 ± 4.8		
PCB-28	2.00 ± 0.24			1.88 ± 0.21		44	19
δ-HCH				0.13 ± 0.01		0.2	
$^{13}C_{12}$-PCB-52					88.9 ± 5.7		
PCB-52	8.1 ± 1.0			8.08 ± 0.9		55	19
$^{13}C_{12}$-PCB-101					88.0 ± 5.1		
PCB-101	34.6 ± 2.6			34.2 ± 3.3		4.4	24
PCB-118	52.1 ± 1.0			49.6 ± 3.9		0.5	19
$^{13}C_{12}$-PCB-153					90.9 ± 5.2		
PCB-153	170 ± 9			175 ± 10		1.4	13
BDE-28		0.8 ± 0.2	0.73 ± 0.07	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
$^{13}C_{12}$-PCB-138					92.2 ± 6.6		
PCB-138	115 ± 13			115 ± 11		1.5	21
$^{13}C_{12}$-PCB-180					94.9 ± 5.5		
PCB-180	74.4 ± 4.0			79.9 ± 3.0		0.03	14
BDE-49				1.81 ± 0.08		0.9	3
BDE-47		31 (2.9	33.5 ± 0.6	33. ± 1.9		3.6	2.5
BDE-66			1.62 ± 0.13	1.69 ± 0.27		1.2	2
$^{13}C_{12}$-BDE-77					93.6 ± 6.1		
BDE-100			9.39 ± 0.89	9.42 ± 0.92		0.9	2
$^{13}C_{12}$-PCB-209					97.9 ± 4.7		
PCB-209	1.30 (0.21			1.31 ± 0.11		0.01	15
BDE-99		19.4 ± 1.8	21.8 ± 0.8	22.3 ± 1.4		1.2	4
$^{13}C_{12}$-BDE-126					96.8 ± 5.9		
BDE-85			0.48 ± 0.10	0.49 ± 0.09		0.2	4
PBB-153			3.37 ± 0.37	3.11 ± 0.32		0.2	
BDE-154			6.56 ± 0.68	6.67 ± 0.73		0.1	2
BDE-153		5.1 ± 0.8	3.34 ± 0.24	3.29 ± 0.40		0.2	2
BDE-138				0.35 ± 0.06		0.7	4
BDE-183		<0.4	0.24 ± 0.02	0.24 ± 0.04		0.2	3
$^{13}C_{12}$-BDE-209					74.2 ± 9.4		
BDE-209				0.93 ± 0.12		63	70

[a]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 ± SD, $n = 5$)

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

nd, not detected.

rable selectivity and lower detection limit, to GC/HR-MS. Using ^{13}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^{-1} level or below, in combination with suitable matrix-selective extraction and analyte-specific cleanup procedures soon.

Acknowledgments

This study was supported financially by the National Natural Science Foundation of China (20475046, 20535020), the National Basic Research Program of China (2003CD415001), and the National 863 Project of China (2006AA06Z404). The loan of the Shimadzu GC-MS QP2010 is gratefully acknowledged. Professor John Hodgkiss is thanked for his assistance with English.

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