

FAST GC MEASUREMENT OF PBDEs USING A GAS CHROMATOGRAPH – HIGH RESOLUTION TIME OF FLIGHT MASS SPECTROMETER

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Introduction

The Polybrominated Diphenyl Ethers (PBDEs) are class of brominated flame retardants (BFRs), and have been widely used in electronic equipment, such as television sets, computers and etc. As the chemical structure of PBDEs is similar to Polychlorinated Biphenyls (PCBs), Polychlorinated dibenzo-p-dioxin, or Polychlorinated dibenzofuran (PCDD/F), the toxicity of PBDE is big concern in the view of not only public health but also environmental pollution. Therefore, there are several regulations about the PBDEs quantity consumed (e.g. RoHS directive in Europe, Stockholm Convention on Persistent Organic Pollutants; POPs Convention).

For several years, the environmental, toxicological and biological investigation about PBDEs or PBDEs contaminants has been investigated all over the world. The several kinds of analysis method are employed for such studies according to the kind of sample. And the Gas Chromatograph-Mass Spectrometer (GC-MS) is mainly used as final detection technique for PBDE. Though there are many kinds of GC-MS instrument in the market, the environmental protection agency of U.S. (EPA) employs the magnet sector type mass spectrometer combined with GC as final detection technique as EPA method 1614⁽¹⁾. This method (EPA 1614) is usually used for environmental samples such as water, soil, sediment, and tissue. This method could achieve high-sensitivity and high selectivity for PBDEs due to the high resolving power of magnet sector type mass spectrometer. However, there are two problems in this method. One is that the magnet sector type mass spectrometer is quite big, expensive and hard to use. And another is that it takes long time to detect the PBDEs from mono-brominated diphenyl ether (mono-BDE) to deca-brominated diphenyl ether (Deca-BDE) due to the conventional GC condition.

Recently, GC-time-of-flight mass spectrometer (GC-TOFMS) becomes popular for analysis of chemical pollutants in environmental and biological samples. The important features of TOFMS are the high-speed data acquisition capability and high resolving power of MS. The high-speed data acquisition capability allows TOFMS combining with Fast-GC technique because Fast-GC technique requires the high-speed data acquisition capability. In addition, full MS spectra during GC measurement are always recorded with high-speed data acquisition condition and high MS resolution condition by using TOFMS. It means that the optimization of SIM grouping condition is not necessary before measurement. And even if the unknown compounds were founded in the samples, it could be identified by using elemental composition estimation capability based on exact mass measurement by high MS resolving power. As the results, the combination of Fast-GC and TOFMS has a possibility to reduce total analysis time of PBDEs dramatically.

Although the high sensitivity and high MS resolution of the magnetic sector type mass spectrometer might be necessary for the sample which is contaminated by PBDEs at very low concentration, the analysis method by the combination method of Fast-GC and TOFMS could be useful as 'Screening method' for chemical product which might include PBDEs in it.

In this study, analysis method by Fast-GC and TOFMS for PBDEs were optimized with the electron ionization (EI). Then, the negative ion chemical ionization (NICI) also investigated combining with Fast-GC and TOFMS technique to improve the sensitivity compared to EI.

Materials and methods

The PBDE analytical standard solution EO-5425 was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). 12 congeners (4,4'-Di-BDE (#15), 2,4,4'-Tri-BDE (28), 2,2',4,4'-Tetra-BDE (#47), 2,2',4,4',5-Penta-BDE (#99), 2,2',4,4',5,5'-Hexa-BDE (#153), 2,2',4,4',5,6'-Hexa-BDE (#154), 2,2',3,4,4',5,6-Hepta-BDE (#183), 2,2',3,3',4,4',6,6'-Octa-BDE (#197), 2,2',3,3',4,4',5,5',6- Nona-BDE(#206), 2,2',3,3',4,4',5,6,6'- Nona-BDE(#207), 2,2',3,3',4,5,5',6,6'- Nona-BDE(#208), and a Deca-BDE(#209)) were included in EO-5425 as nonane solution. ¹³C-Labeled PBDEs of same 12 congeners were also included as internal standard.

Mass spectrometer was calibrated by using perfluorokerosene (PFK) before measurement for both of EI and NICI.

After measurement, the m/z values of all EI data were compensated by using of polysiloxane peak (m/z 281.0517; $C_7H_{21}O_4Si_4$) as the known compound because the polysiloxane was continuously eluted from the liquid phase of capillary column. The m/z values for NICI data were compensated by using Cl_2 (m/z 69.9377). Aldrin and dieldrin were spiked to EO-5425 standard solution as internal standard compounds for NICI.

All standard solutions were measured by a JMS-T100GC V "AccuTOF GCv" (JEOL Ltd.). The MS resolving power of JMS-T100GCV is 6,000 for EI and NICI. All data were acquired as profile spectra, then those were converted to centroided spectra before quantitative operation.

The measurement conditions for PBDEs are shown in Table 1.

Instrument	JMS-T100GCV "AccuTOF GCv" (JEOL Ltd.)
Injection mode	Splitless
Inlet temp.	270°C
Column	DB-1HT (Length 15m, I.D. 0.25mm, film thickness 0.1 μm)
Oven temp.program	140°C (2min) => 45°C /min => 340°C (3min), Total ; 9.44 min
Sample injection volume	1 μL
Carrier gas	He (1.4 mL/min)
Ionization mode	EI+; 38 eV, 300μA CI(-); 200eV, 300μA, Methane gas (1.2 mL/min)
Chamber temp.	300 °C
GC/MS interface temp.	300 °C
m/z range	50 - 1,000
Data acquisition speed	0.1 sec (10Hz)

Results and discussion:

Mass spectra of Deca-BDE (#209) using EI mode (Top) and NICI mode (Bottom) were shown Fig.1. In the case of EI, intensity of molecular ion $[M]^+$ was the secondly highest in the spectrum. In the case of Penta-BDE, Hexa-BDE, Hepta-BDE, Octa-BDE, Nona-BDE, and Deca-BDE, $[M-Br_2]^+$ ion peak was highest. Therefore the ions derived from $[M-Br_2]^+$ were selected as the quantitative ions. In the case of NICI, no molecular ion was detected, and bromine ion $[Br]^-$ was detected as base peak. $[C_6OBr_5]^-$ ion was also detected, however the relative intensity of $[C_6OBr_5]^-$ was very small. For quantitative analysis by NICI, m/z 78.9183 and 80.9163 ions derived from bromine ion were selected.

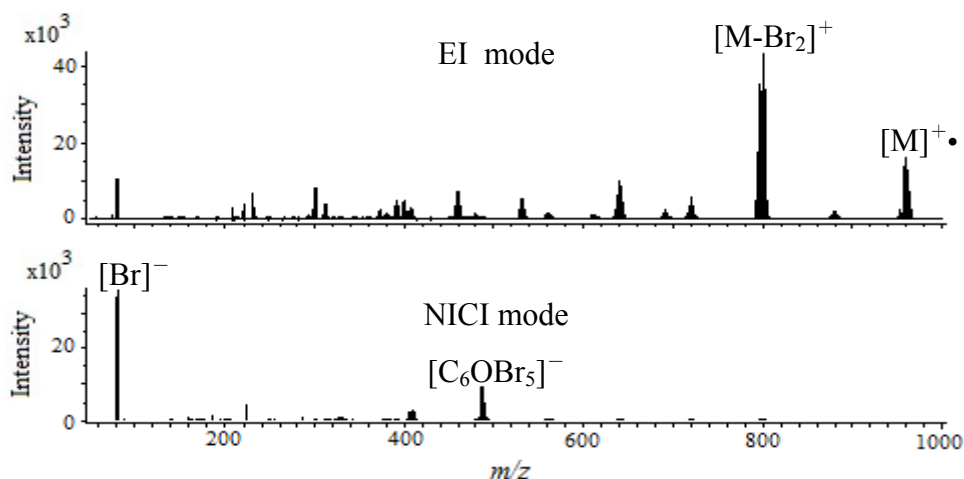


Fig.1 Mass spectra of Deca-BDE (EI mode; Top, NICI mode; Bottom).

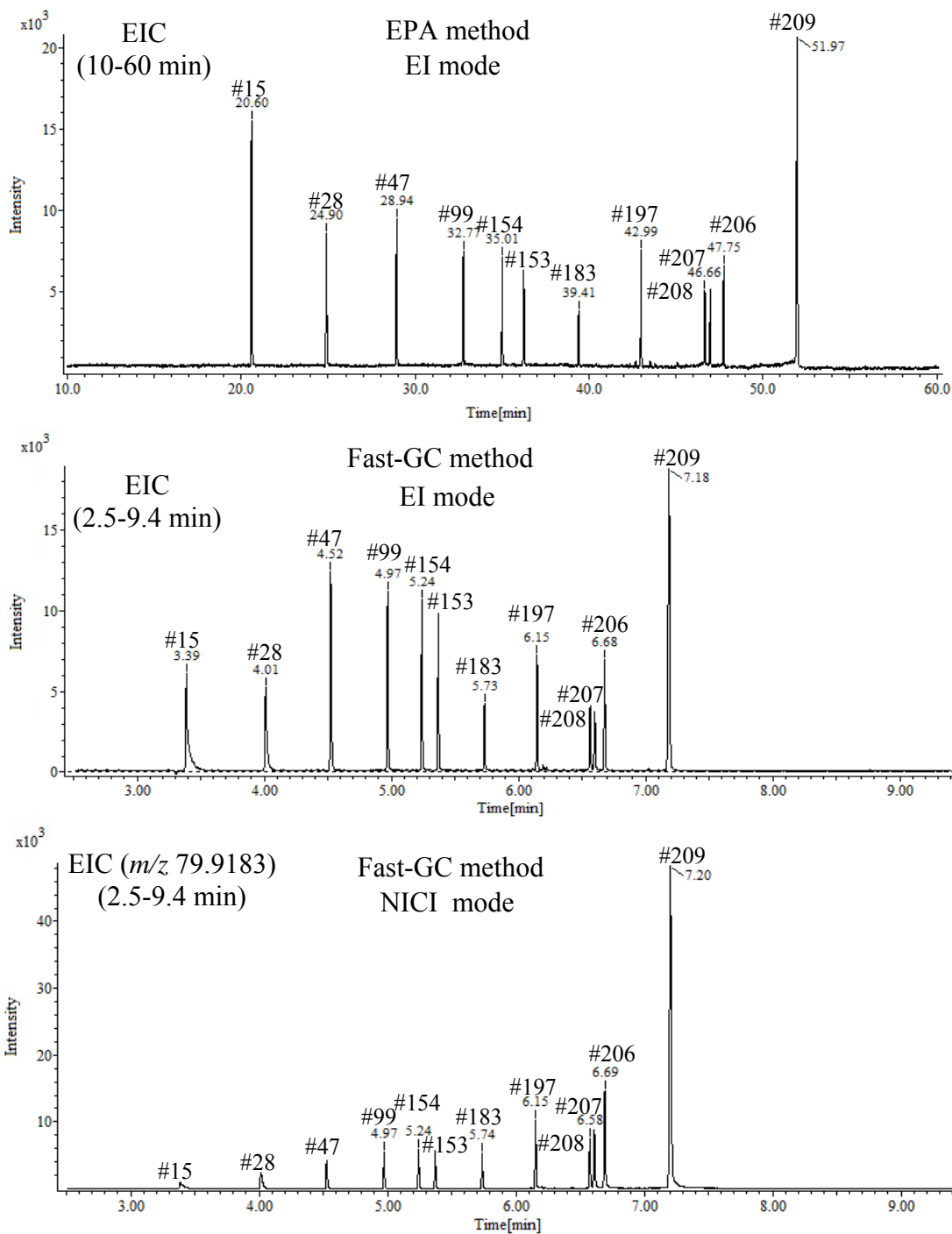


Fig.2 Extracted ion chromatograms of PBDEs using EPA GC method (EI mode; Top) and Fast-GC method (EI mode; Middle, NICI mode; Bottom).

Standard solution was measured with the condition of EPA 1614 method, Fast-GC (EI) and Fast-GC (NICI). The extracted ion chromatograms (EICs) for each method were shown in fig. 2. EICs from EPA 1614 method and Fast-GC (EI) method were created as the summation chromatogram of each EIC for all congeners. The EIC

of bromine ion (m/z 79.9183) were shown because all congeners of PBDEs were monitored as bromine ion (m/z 79.9183) for Fast-GC (NICI). All peaks of PBDEs were assigned according to reference [2] and [3].

Comparing between the EICs by EPA 1614 method and the EICs by Fast-GC (EI), the total time for elution of all congeners of PBDEs were dramatically reduced from 52 minutes to less than 10 minutes although the relative retention time of each peak was similar. Also, the relative peak intensity among each isomer was almost same between EPA 1614 and Fast-GC (EI) because both methods employed the same ionization method (EI). On the other hand, the relative peak intensity of among each isomer for Fast-GC (NICI) was different from EPA 1614 or Fast-GC (EI). In case of NICI, the sensitivity of PBDEs which has large number of bromine atoms in inside of molecule was higher than PBDEs with small number of bromine atoms.

The measurement results of standard solution were summarized in table 2 and 3 for Fast-GC (EI) method and Fast-GC (NICI). In the case of Fast-GC (NICI), the standard solution at ten times lower concentration than Fast-GC (EI) were measured. The reproducibility of the absolute peak area or relative peak area of each congener was almost same between table 2 and 3. It means that the sensitivity of PBDEs by Fast-GC (NICI) method were ten times higher than Fast-GC (EI) method. As mentioned before, the sensitivity of PBDEs is dependent on the number of bromine in inside of molecule. For those reasons, the sensitivity of DiBDE by Fast-GC (NICI) was same or slightly lower than Fast-GC (EI). However, the sensitivity of DeBDE by Fast-GC (NICI) was almost hundred times higher than Fast-GC (EI). Fast-GC (NICI) method has enough sensitivity for PBDEs.

As the chemical products such as plastic products will include the DeBDE mainly, Fast-GC (NICI) method will be useful for rapid screening of PBDEs in the chemical products.

Table 2. Each congener quantitative ions, reference ions and results for Fast-GC EI data.

Compound name	BDE No.	Exact mass (EI)		Concentration of STD (pg/ μ L)	Absolute area (n=5)			Relative area (n=5)		
		Quantitative ion	Reference ion		Average area	S.D.	C.V.(%)	Average area	S.D.	C.V.(%)
DiBDE	#15	327.8922	325.8942	10	5766	298.6	5.2	1.174	0.022	1.88
TriBDE	#28	405.8027	407.8007	10	2724	143.1	5.3	0.997	0.021	2.08
TeBDE	#47	485.7112	483.7132	10	2620	169.3	6.5	0.992	0.034	3.38
PeBDE	#99	403.7870	405.7850	10	1828	110.1	6.0	0.977	0.034	3.44
HxBDE	#154	483.6955	481.6975	10	1619	113.8	7.0	0.827	0.032	3.88
	#153			10	1470	104.8	7.1	0.822	0.039	4.74
HpBDE	#183	561.6060	563.6040	10	850	52.4	6.2	1.030	0.036	3.49
OcBDE	#197	641.5145	639.5165	25	1783	98.9	5.5	0.976	0.045	4.56
NoBDE	#208	719.4250	721.4230	25	1168	107.0	9.2	1.043	0.087	8.30
	#207			25	1132	111.7	9.9	1.006	0.079	7.85
	#206			50	1622	88.7	5.5	1.079	0.044	4.09
DeBDE	#209	799.3335	797.3355	100	1744	245.0	14.0	0.192	0.017	8.68

Table 3. Each congener quantitative ions, reference ions and results for Fast-GC NICI data.

Compound name	BDE No.	Exact mass (NICI)		Concentration of STD (pg/ μ L)	Absolute area (n=5)			Relative area (n=5)		
		Quantitative ion	Reference ion		Average area	S.D.	C.V.(%)	Average area	S.D.	C.V.(%)
DiBDE	#15	78.9183	80.9163	1	510	57.1	11.2	0.193	0.020	10.49
TriBDE	#28			1	917	81.9	8.9	0.347	0.033	9.64
TeBDE	#47			1	902	77.0	8.5	0.341	0.030	8.93
PeBDE	#99			1	960	51.0	5.3	0.362	0.018	5.02
HxBDE	#154			1	1081	50.5	4.7	0.409	0.024	5.86
	#153			1	1051	26.9	2.6	0.397	0.012	2.94
HpBDE	#183			1	863	61.1	7.1	0.326	0.028	8.52
OcBDE	#197			2.5	1576	93.8	6.0	0.595	0.037	6.28
	#208			2.5	997	34.3	3.4	0.377	0.017	4.55
NoBDE	#207			2.5	1365	30.1	2.2	0.516	0.020	3.79
	#206			5	2061	68.7	3.3	0.778	0.023	2.92
DeBDE	#209			10	14108	570.9	4.0	5.320	0.250	4.70

References:

1. U.S. EPA. Method 1614. (2007).
2. Ethel Eljarrat, Agustina de la Cal, Damià Barceló. (2003); *J. Chromatogr. A* 1008 : 181-192.
3. W. Qu, X. Bi, G. Sheng, S. Lu, J. Fu, J. Yuan, L. Li. (2007); *Environ Int.* 33: 1029-1034.