Analysis Method of Polybrominated Diphenyl Ethers Using GC-MS and GC-MS/MS Coupled With an Automated Identification and Quantitation System with a Database

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Introduction

There are 209 isomers of polybrominated diphenyl ethers (PBDE), each with varying levels of toxicity and detection frequency in environmental samples. A common method for analysis of PBDEs requires expensive C13-labeled standards and a gas chromatograph coupled to a high resolution magnetic sector mass spectrometer (GC-HRMS). The operation of GC-HRMS instruments requires a highly skilled analyst, and maintenance can be time-consuming and labor-intensive. This poses a critical situation, especially for environmental laboratories in developing countries.
 Kadokami et al. [1] developed a novel automated identification and semi-quantitation database (AIQS-DB) which allows automatic identification and semi-quantitation of 1,000 pollutants without requiring analysis of standards. The database includes retention indices, mass spectra, and internal calibration curves for 1,000 environmental pollutants. The pollutants are

identified using the mass spectrum and retention time (RT) predicted by retention index. Semi-quantitation is performed using internal calibration curve.
This poster illustrates a method for analysis of PBDE using the database. To minimize the use of costly internal standards, the AIQS-DB was applied to PBDE with lower toxicity and detection frequency, while the conventional method (isotope dilution) was applied to PBDEs with a higher toxicity and detection frequency to obtain precise quantitation results. Single quadrupole GC-MS could be used for some samples, however the sediment samples had complex, interfering co-extractants which hindered detection of the PBDE. Samples with interfering matrices were analyzed on a triple quadrupole GC-MS/MS. Using the GC-MS/MS, the PBDE were successfully identified, and analysis results corresponded to concentrations of PBDE determined by the conventional HR-GCMS method.

1. Novel gas chromatography-mass spectrometry database for automatic identification and quantification of micropollutants, Kiwao Kadokami, Kyoko Tanada, Katsuyuki Taneda, Katsyhiro Nakagawa, *J. Chromatogr A*, 1089 pp 219-226, 2005.

Results

Evaluation of AIQS-DB

Accuracy of predicated RT was evaluated using analytical standards with three different GC-MS instruments, and a real sample.

Table 1 Accuracy of prediction RT for standards on three different instruments (A, B, and C)

Compound	ΔRT [min]		
	A	B	C
Tri/ BDE-028	0.04	-0.07	-0.03
Tetra/ BDE-47	0.05	-0.06	-0.02
Penta/ BDE-100	0.08	-0.03	0.01
Penta/ BDE-99	0.07	-0.04	0.00
Hexa/ BDE-154	0.08	-0.03	0.00
Hexa/ BDE-153	0.08	-0.02	0.01
Hepta/ BDE-183	0.09	-0.03	0.00
Deca/ BDE-209	0.08	-0.04	-0.01

ΔRT=predicted - measured RT

Table 2 Accuracy of prediction RT for real sample

Compounds	ΔRT [min]
Tri/ BDE-028L	0.09
Mono/ BDE-001	0.09
Di/ BDE-010	0.08
Tri/ BDE-028	0.08
Tetra/ BDE-47L	0.12
Tetra/ BDE-51	0.09
Penta/ BDE-99L	0.14
Penta/ BDE-105	0.13
Hexa/ BDE-153L	0.03
Hexa/ BDE-140	0.08
Hepta/ BDE-183L	0.07
Hepta/ BDE-190	0.11

Semi-quantitation results for sediment sample spiked with PBDEs at 50 ng/mL.

Compounds	Conc.
Mono/ BDE-001	64.2
Di/ BDE-010	64.0
Tri/ BDE-028	68.5
Tetra/ BDE-51	62.9
Penta/ BDE-105	53.7
Hexa/ BDE-140	60.7
Hepta/ BDE-190	169.9

ng/mL

• The maximum difference in RT was 0.14 min.

• Semi-quantitation results were from 68.5 to 53.7 ng/mL, except hepta/ PBDE-190.

• PBDE-190 co-eluted with an interference and could not be accurately quantified

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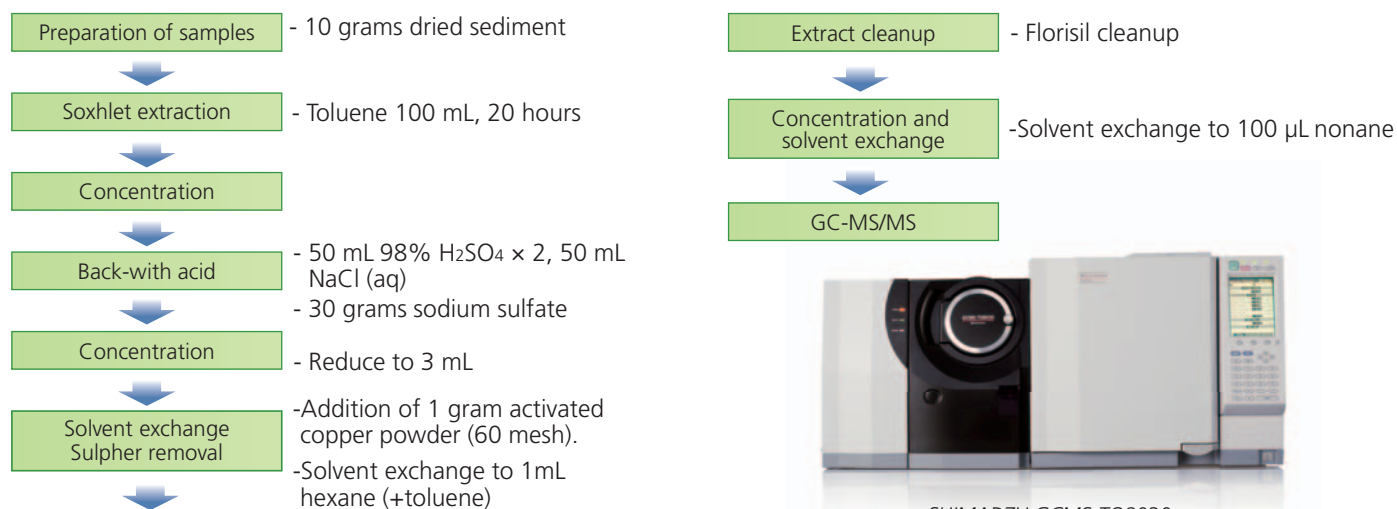
Experimental

Target compounds

Conventional method

ID	Compound	IS^{13}C$_{12}$
1	Tri/ BDE-028	Tri/ BDE-028L
2	Tetra/ BDE-47	Tetra/ BDE-47L
3	Penta/ BDE-99	Penta/ BDE-99L
4	Penta/ BDE-100	Penta/ BDE-100L
5	Hexa/ BDE-153	Hexa/ BDE-153L
6	Hexa/ BDE-154	Hexa/ BDE-154L
7	Hepta/ BDE-183	Hepta/ BDE-183L
8	Deca/ BDE-209	Deca/ BDE-209L

AIQS-DB

ID	Compound	ID	Compound	ID	Compound	ID	Compound
9	Mono/ BDE-001	19	Tri/ BDE-017	29	Tetra/ BDE-066	39	Penta/ BDE-120
10	Mono/ BDE-002	20	Tri/ BDE-025	30	Tetra/ BDE-071	40	Penta/ BDE-126
11	Mono/ BDE-003	21	Tri/ BDE-028	31	Tetra/ BDE-075	41	Hexa/ BDE-128
12	Di/ BDE-007	22	Tri/ BDE-030	32	Tetra/ BDE-077	42	Hexa/ BDE-138
13	Di/ BDE-008	23	Tri/ BDE-032	33	Tetra/ BDE-079	43	Hexa/ BDE-140
14	Di/ BDE-010	24	Tri/ BDE-033	34	Penta/ BDE-085	44	Hexa/ BDE-155
15	Di/ BDE-011	25	Tri/ BDE-035	35	Penta/ BDE-105	45	Hexa/ BDE-156
16	Di/ BDE-012	26	Tri/ BDE-037	36	Penta/ BDE-116	46	Hepta/ BDE-181
17	Di/ BDE-013	27	Tetra/ BDE-049	37	Penta/ BDE-118	47	Hepta/ BDE-190
18	Di/ BDE-015	28	Tetra/ BDE-051	38	Penta/ BDE-119		

Sample preparation

| Preparation of samples | - 10 grams dried sediment |

Soxhlet extraction — Toluene 100 mL, 20 hours

Concentration

Back-with acid — 50 mL 98% H_2SO_4 × 2, 50 mL NaCl (aq); - 30 grams sodium sulfate

Concentration — Reduce to 3 mL

Solvent exchange Sulpher removal — Addition of 1 gram activated copper powder (60 mesh). Solvent exchange to 1mL hexane (+toluene)

Extract cleanup — Florisil cleanup

Concentration and solvent exchange — Solvent exchange to 100 μL nonane

GC-MS/MS

SHIMADZU GCMS-TQ8030

GC-MS/MS Analysis

Table 4 Repeatability of the analysis (n=5; 10 ng/mL, Deca-BDE: 100 ng/mL) and linearity of calibration curve (10, 20, 50, 100, 500 ng/mL (Deca BDE; X10)

Compounds	StDev	%RSD	R	Compounds	StDev	%RSD	R
Tri/ BDE-028	0.2355	2.40	0.99999	Hexa/ BDE-154	0.247	2.43	0.99997
Tetra/ BDE-47	0.4045	4.01	0.99993	Hexa/ BDE-153	0.210	2.14	0.99998
Penta/ BDE-100	0.4639	4.65	0.99997	Hepta/ BDE-183	0.591	5.84	0.99997
Penta/ BDE-99	0.3707	3.77	0.99998	Deca/ BDE-209	3.664	3.94	0.99962

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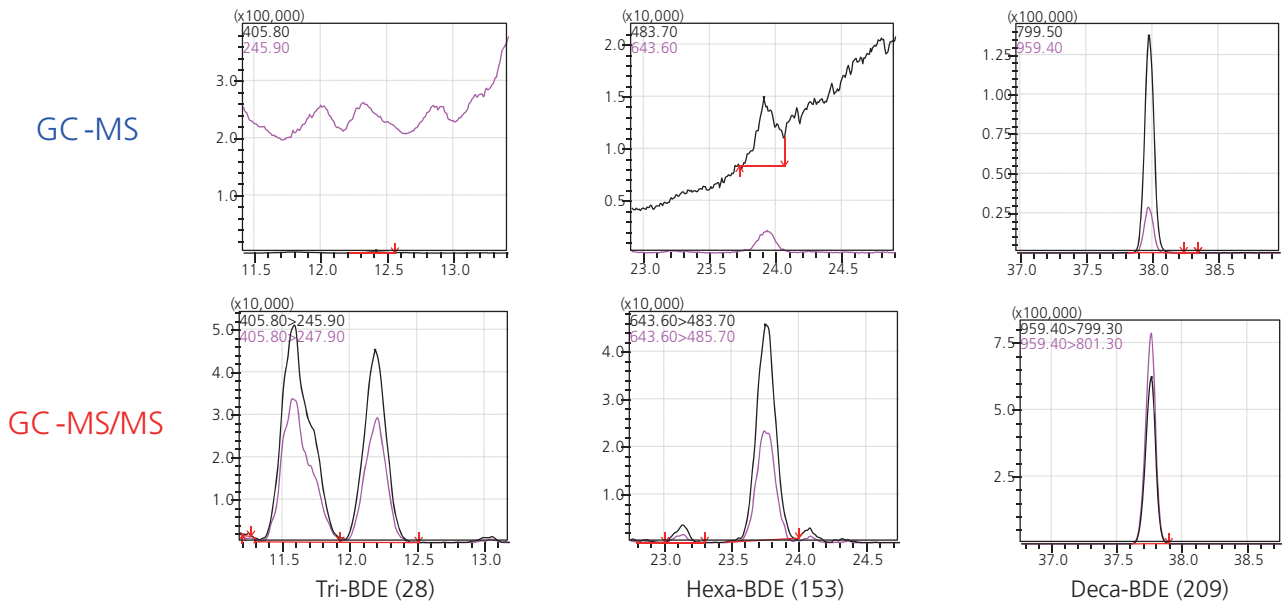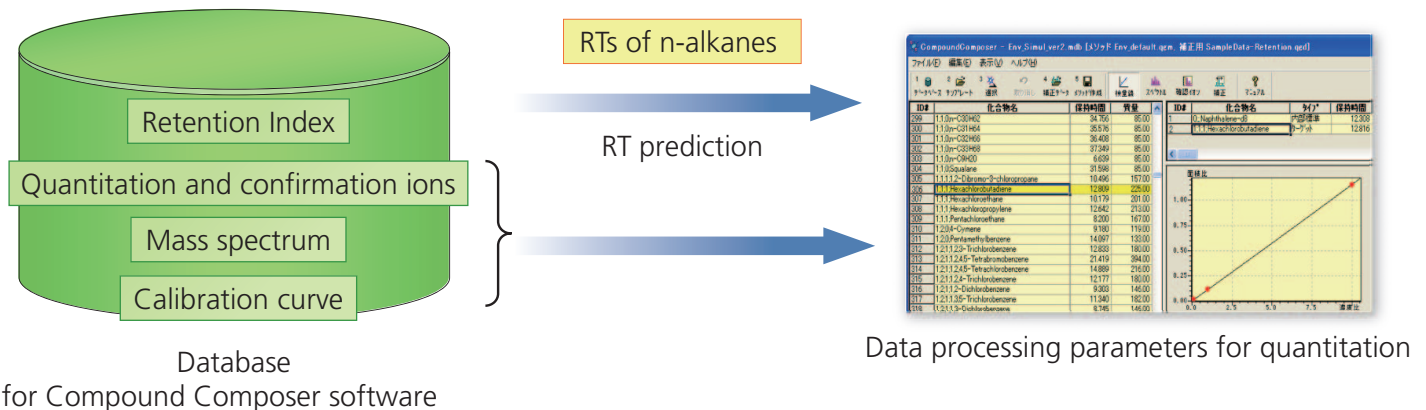

Fig. 1 Chromatograms of selected PBDEs in sediment using GC-MS and GC-MS/MS

Analytical conditions

GC-MS : **GCMS-TQ8030**

Column	:Rtx - 1614 (15 m × 0.25 mm I.D., 0.10 mm)	Ion Source Temp.	:230°C
Injection Mode	:Splitless	Interface Temp.	:300°C
Sampling Time	:1 min	Solvent Cut Time	:1 min
Injection Volume	:1 μL	Ionization Voltage	:70 eV
Injection Temp.	:320°C	Emission Current	:150 μA
Column Oven Temp.	:140°C (3 min), 5°C /min to 320°C (5 min)	Acquisition Mode	:SIM (GC-MS)
Carrier Gas	:He		MRM (GC-MS/MS)
Flow Control Mode	:Linear Velocity (47.9 cm/sec)		
Purge Flow	:5 mL/min		
High Pressure Injection	:150 kPa (1.2 min)		

AIQS-DB

Database
for Compound Composer software

Data processing parameters for quantitation

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Table 5 Comparison of quantitation results of PBDEs in sediment using GC-MS, GC-MS/MS, and GC-HRMS

BDE-**	Tri 28	Tetra 47	Penta 100	Penta 99	Hexa 154	Hexa 153	Hepta 183	Deca 209 [ng/g]
GC-MS	0.45	4.89	1.51	6.45	0.78	1.77	1.88	112.58
GC-MS/MS	0.52	4.94	1.55	6.39	0.92	1.84	1.90	104.10
GC-DMS	0.48	4.78	1.35	6.19	0.93	1.90	2.04	99.45

Gas chromatography–triple quadrupole mass spectrometry (GC-MS/MS) was applied to the analysis of PBDEs in a complex sediment sample matrix, ensuring accurate identification and low-level detection. Using the GC-MS/M, the PBDE were successfully identified, and analysis results corresponded to concentrations of PBDE determined by the conventional HR-GCMS method.

Conclusion

1. To minimize the use of costly internal standards, the AIQS-DB was applied to PBDE with lower toxicity and detection frequency, while the conventional method (isotope dilution) was applied to PBDEs with a higher toxicity and detection frequency to obtain precise quantitation results.
2. For complex matrices such as sediment, GC-MS/MS was used to selectively detect PBDE in the presence of co-extractants.
3. The results show that the developed method can be applied to analysis of PBDE in sediment.

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