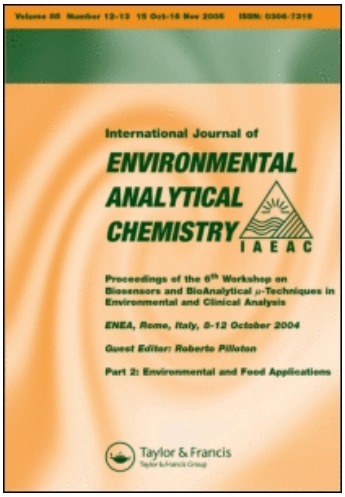

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Optimisation of the analytical method for octa-, nona- and deca-brominated diphenyl ethers using gas chromatography-quadrupole mass spectrometry and isotope dilution

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Online publication date: 14 March 2011

To cite this Article Eguchi, Akifumi , Isobe, Tomohiko , Ramu, Karri and Tanabe, Shinsuke(2011) 'Optimisation of the analytical method for octa-, nona- and deca-brominated diphenyl ethers using gas chromatography-quadrupole mass spectrometry and isotope dilution', International Journal of Environmental Analytical Chemistry, 91: 4, 348 — 356
To link to this Article: DOI: 10.1080/03067319.2010.496040
URL: http://dx.doi.org/10.1080/03067319.2010.496040

Intern. J. Environ. Anal. Chem.
Vol. 91, No. 4, 10 April 2011, 348–356

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Optimisation of the analytical method for octa-, nona- and deca-brominated diphenyl ethers using gas chromatography–quadrupole mass spectrometry and isotope dilution

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(*Received 8 September 2009; final version received 17 May 2010*)

An analytical method for higher brominated congeners of polybrominated diphenyl ethers (PBDEs) was optimised using a gas chromatograph equipped with an electron impact ionisation-quadrupole mass spectrometer (GC-EI-qMS) and five native PBDEs and three $^{13}C_{12}$-labelled congeners in biological and environmental samples (mussels, sediment, dust). In the optimised instrumental conditions, abundance and repeatability improved with increase in temperature of the ion source. The instrumental detection limits (IDLs) for BDE-196, BDE-197, BDE-206, BDE-207 and BDE-209 were 0.1, 0.1, 0.2, 0.3 and 0.6 pg, respectively. When compared to the previous reports, the IDLs were the same as for electron capture negative ionisation (ECNI) or EI-double focusing magnetic sector (EI-Sector) mass spectrometer, indicating that sensitive determination could be achieved using a conventional GC-EI-qMS. Validation of the method was carried out by the analysis of reference materials and mussel samples. We confirmed that the concentrations quantified using this method was in the range of reported values for reference materials. Similar concentrations were found in mussels, which were analysed previously by our group. Thus, we conclude that a conventional GC-EI-qMS can be applied for analysis of higher brominated PBDEs in various environmental and biota matrices.

Keywords: gas chromatography-quadrupole mass spectrometry, BDE-209, electron impact ionisation

1. Introduction

Brominated flame retardants (BFRs) are synthetic compounds which have been widely used to decrease the likelihood and intensity of fire in a variety of consumer products, such as automobile accessories, computers, foam furniture, building material, electrical and electronic appliances and textiles [1]. Because of their similarity in environmental fate, and toxic potencies with polychlorinated biphenyls (PCBs), environmental contamination and bioaccumulation of PBDEs are of concern. Several studies have suggested that PBDEs could cause neurobehavioural changes, affect foetal development and possibly cause cancer in laboratory animals and act as endocrine disrupters [2]. There are three major

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ISSN 0306–7319 print/ISSN 1029–0397 online

DOI: 10.1080/03067319.2010.496040
http://www.informaworld.com

commercial PBDE mixtures and the total world market demand for those penta-, octa- and deca-BDEs were 56100, 3790, 7500 metric tons, respectively, in 2001 [3,4]. Currently, deca-BDE (BDE-209) is the most widely used commercial PBDE flame retardant [5]. BDE-209 has been detected at high concentrations in house dust, sediment and soil [6–8]. Several studies suggested that BDE-209 can be degraded or metabolised to relatively more toxic lower brominated congeners [9–11]. In general, bioaccumulation and toxicological potential of PBDEs increase with decrease in number of bromine atoms. Therefore, studies on environmental distribution and behaviour of BDE-209 are essential. Some analytical methods, which employed mainly double focusing magnetic sector (Sector)-MS [12–14], electron capture negative ionisation (ECNI)-MS [15,16], or electron capture detector (ECD) [17], have already been designed and applied to environmental samples. The earlier methods, however, have some limitations for comprehensive routine analysis. Although Sector-MS can provide sensitive and selective data, instruments are extremely expensive for routine and high through-put analysis and require technical skills for operation. ECNI-MS is a sensitive instrument, especially for halogenated compounds. However, spiking with labelled internal standards cannot be applied when halogen atom is used as a quantifier ion in ECNI-MS. ECD is also sensitive and easy to handle, but complete purification these samples and chromatographic separation of individual substances is needed and labelled so internal standard cannot be spiked. Recently, linear ion trap (LIT)-MS [18], inductively coupled plasma (ICP)-MS [19] and triple quadrupole-MS [20] have also been proposed as selective and sensitive analytical tools for higher brominated PBDEs. Unfortunately, all of the instruments are neither cheap nor commonly used. In this regard, a sensitive, selective, simple and robust analytical method using a conventional analytical instrument is required to conduct comprehensive monitoring surveys. A gas chromatograph equipped with an electron impact ionisation-quadrupole mass spectrometer (GC-EI-qMS) is one of the most commonly used analytical instruments in environmental chemistry. It has been applied in the analysis of numerous contaminants in various environmental matrices including mono- to hepta-PBDEs [15,21]. In addition, EI mode allows the use of $^{13}C_{12}$-labelled internal standards for a more precise determination of the target compounds. It has, however, been recognised that GC-EI-qMS is not sensitive for higher brominated, i.e. octa- to deca-brominated, PBDEs due to their high molecular weight and low volatility [22]. In the present study, analytical conditions were optimised for various environmental matrices and validated by certified reference material for the analysis of higher brominated PBDEs.

2. Experimental

2.1 *Chemical regents and standard solutions*

Dichloromethane, hexane, acetone, isooctane, methanol, H_2SO_4, HCl and anhydrous sodium sulphate were purchased from Wako Pure Chemical Industries (Tokyo, Japan) and Nacalai Tesque (Osaka, Japan). Silica gel, 2% (w/w) KOH-silica gel, 22% (w/w) H_2SO_4-silica gel and 44% (w/w) H_2SO_4-silica gel were obtained from Wako Pure Chemical Industries (Tokyo, Japan). Native PBDE standards, including BDE-196, BDE-197, BDE-206, BDE-207 and BDE-209, and labelled internal standards, including $^{13}C_{12}$-BDE-197, $^{13}C_{12}$-BDE-207 and $^{13}C_{12}$-BDE-209, were purchased from Wellington Laboratories (Guelph, Ontario, Canada).

2.2 *Samples*

Standard reference materials for organic contaminants in house dust (NIST SRM2585) was obtained from National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). A certified sediment sample (NIES CRM Air Dried Sediment#1), which was prepared for an inter-laboratory calibration exercise, was provided by National Institute for Environmental Studies (NIES, Tsukuba, Japan) [23]. Samples of green mussels (*Perna viridis*) and blue mussels (*Mytilus edulis*), were collected in 2003–2005 from various locations in Asia [14].

2.3 *Sample extraction and clean up*

PBDEs were analysed following the procedure described elsewhere with some modifications [24]. Approximately 1 g dry sediment was placed in a conical flask and spiked with surrogates including each 5 ng of $^{13}C_{12}$-BDEs ($^{13}C_{12}$-BDE-197, BDE-207 and BDE-209). $^{13}C_{12}$-BDE-197 was used to quantify octa-brominated BDEs, $^{13}C_{12}$-BDE-207 for nona-brominated BDEs and $^{13}C_{12}$-BDE-209 for deca-brominated BDE. Extraction was carried out using 50 ml of hexane/acetone (50 : 50, v/v) using an electric shaker (SR-2W, TAITEC, Saitama, Japan) at 260 rpm for 15 min and centrifuged at 2500 rpm for 15 min. The supernatant was transferred to a glass flask. The sample residue was further extracted with hexane/acetone (50 : 50, v/v) by ultrasonic bath (EYELA, Tokyo, Japan), centrifuged and the extract was transferred to the same flask containing the primary extract. Sonication was repeated twice and all the extracts were combined. The extract was added on to a multilayer silica gel column, composed of 1 g anhydrous sodium sulphate, 6 g of 22% sulphuric acid silica gel, 2 g 44% sulphuric acid silica gel, 0.5 g silica gel, 3 g 2% KOH silica gel and 0.5 g silica gel, sequentially from top to bottom. PBDEs were eluted by 150 ml of hexane/DCM (75 : 25, v/v). The hexane/DCM eluate was then purified with concentrated sulphuric acid. After acid treatment, the solution was exchanged into hexane/DCM and passed though gel permeation chromatography (GPC) for clean up. GPC column was composed of 50 g BioBeads S-X3 (BioRad). Elution solvent was hexane/DCM (1 : 1, v/v). The first 130 ml fraction was discarded, and the following 150 ml containing PBDEs were collected and solvent exchanged into hexane. The GPC fraction containing analytes was fractionated by 4 g activated silica gel column with 80 ml 5% dichloromethane in hexane for clean up. Sediment extracts were treated with activated copper (activated by H_2O/HCl, 1 : 4, v/v) to remove sulphur. Extraction of house dust was carried out by toluene using high speed solvent extractor (SE-100, Mitsubishi Chemical Analytech, Mie, Japan). Conditions of the extractor were as follows; flow rate: 6 ml/min, extraction temperature: 80°C, extraction time: 1 hour. An aliquot of the extract, after spiking internal standards as a clean up spike for recovery calibration was also cleaned up as mentioned above.

For mussel samples, 2–3 g of the freeze dried sample was ground with anhydrous sodium sulphate and extracted in a Soxhlet apparatus with a mixture of hexane/diethyl ether (25 : 75, v/v) for 7–8 h. An aliquot of the extract, after adding 5 ng of internal standards was exchanged into hexane/DCM and added to a GPC column GPC column was composed of 50 g BioBeads S-X3 (BioRad) for lipid removal. Elution solvent was hexane/DCM (1 : 1, v/v). The first 130 ml fraction was discarded, and the following 150 ml containing PBDEs were collected and solvent exchanged into hexane. The GPC fraction containing analytes was fractionated by 4 g activated silica gel column with 80 ml 5%

dichloromethane in hexane for clean up. $^{13}C_{12}$-labelled BDE-139 was spiked to the final solution as a syringe spike for response calibration prior to GC-EI-qMS analysis.

2.4 *Instrumentation*

Identification and quantification were performed using an Agilent 7980A GC coupled with an Agilent 5975C MS. GC separation was achieved by a DB-1MS fused silica capillary column (Agilent, Tokyo, Japan.) of 15 m length × 0.25 mm i.d. × 0.1 μm film thickness. The injector temperature was 260°C and it was operated in a pulsed splitless mode (pressure pulse, 40 psi/2 min). GC oven program was as follows; initial temperature of 80°C (held for 2 min) was raised to 300°C at 20°C min^{-1} and then held for 17 min. The transfer line was held at 310°C. PBDEs were monitored in selective ion monitoring (SIM) mode. The following ions were monitored: $[M\text{-}2Br+4]^+$, $[M\text{-}2Br+6]^+$, $[M\text{-}2Br+8]^+$ for Octa, Nona-BDE, $^{13}C_{12}$-Octa, and $^{13}C_{12}$-Nona-BDE, and $[M\text{-}2Br+6]^+$, $[M\text{-}2Br+8]^+$, $[M\text{-}2Br+10]^+$ for Deca-BDE and $^{13}C_{12}$-Deca-BDE (Table 1). Detailed information on the analytical conditions is described elsewhere [25,26].

3. Results and discussion

3.1 *Optimisation of instrumental conditions*

Temperature of GC injection port and ion source of MS was optimised. For BDE-209, the highest peak abundance was observed at injection port temperature of 260°C. The peak abundance at lower temperature, i.e. 240°C, was about 10% less than that at higher temperature. Relative standard deviation (RSD) of peak area for 5 replicate injections improved from 10% at 240°C to 5% at 260°C. Based on this, we set the injection port temperature at 260°C, since thermal decomposition of BDE-209 was reported

Table 1. GC-EI-qMS operating conditions for the analysis of higher brominated PBDEs.

Compound name	Retention time (min)	Quantifier ion (m/z)	Qualifier ion (m/z)	Recovery (%)	IDL (pg)	MDL soil and dust (pg/g dry)	MDL mussel (pg/g lipid)
BDE-196	11.50–13.00	641.5	639.5, 643.5	–	0.1	2.0	8.0
BDE-197	11.50–13.00	641.5	639.5, 643.5	–	0.1	2.0	8.0
BDE-206	13.00–14.00	719.4	717.4, 721.4	–	0.3	2.6	10
BDE-207	13.00–14.00	719.4	717.4, 721.4	–	0.2	3.1	15
BDE-209	14.00–30.00	799.3	797.3, 801.3	–	0.6	70	500
$^{13}C_{12}$-BDE-139	7.00–11.50	655.6	653.6, 657.6	–			
$^{13}C_{12}$-BDE-197	11.50–13.00	653.6	651.6, 655.6	96.6 ± 2.4			
$^{13}C_{12}$-BDE-207	13.00–14.00	731.5	729.5, 733.5	92.4 ± 1.7			
$^{13}C_{12}$-BDE-209	14.00–30.00	811.4	809.4, 813.4	77.8 ± 3.0			

The congeners in each homologue group include Octa-BDE: BDE-196, -197; Nona-BDE: BDE-206, -207; Deca-BDE: BDE-209; $^{13}C_{12}$-Octa-BDE: $^{13}C_{12}$-BDE-197; $^{13}C_{12}$-Nona-BDE: $^{13}C_{12}$-BDE-207; $^{13}C_{12}$-Deca-BDE: $^{13}C_{12}$-BDE-209.

Instrumental detection limit IDL was defined as 3 times the standard deviation (SD) of 5 replicate injections of a low concentration standard solution (2.5 pg/μl). Method detection limit (MDL) was defined as 3 times the peak area in the blank sample.

at 300°C or higher [27]. In addition, the temperature of ion source was also optimised. The ion source temperature was raised from 180 to 350°C [26]. The peak shape gradually improved with the increase in ion source temperature. Reduction of peak width and tailing was accompanied by an increase in peak height. Higher ion source temperature could be better for higher brominated PBDEs as their high boiling points are higher. Peak area also increased with the ion source temperature (Figure 1). Peak area of BDE-209 at 320°C or above, (relatively stable in the temperature range) was about 2 times higher than that at 180 and 240°C, indicating that the sensitivity is greater at the higher ion source temperatures. Furthermore, variation in the peak area of the 5 replicate injections, represented as relative standard deviation (RSD), decreased from 10% at 180°C to 5% at 320°C. Reduced variation is essential for reliability and repeatability of the analytical method. Therefore, the temperature of the ion source was set at 320°C.

3.2 *Sensitivity and reliability of the method*

Instrumental detection limit (IDL) was defined as 3 times the standard deviation (SD) of 5 replicate injections of a low concentration standard solution (2.5 pg/μl). The IDLs were 0.1, 0.1, 0.3, 0.2 and 0.6 pg for BDE-196, 197, 206, 207 and 209, respectively (Table 1). In addition, variation in the peak areas represented as the RSD for 5 replicate injections were 2.5, 4.5, 2.6, 1.6 and 4.7% for BDE-196, 197, 206, 207 and 209, respectively, for GC-EI-qMS. This was also better than RSD of BDE-209 for bench top GC-EI-Sector-MS, which was 29%. Method detection limit (MDL) was defined as three times the peak area of the blank sample that was analysed with every batch of samples (usually 7 samples and one blank). The MDLs of the GC-EI-qMS for higher brominated PBDE were 2.0–70 pg/g dry wt in soil and house dust and 0.8–50 pg/g dry wt in mussel samples (Table 1). The IDL for BDE-209 in the present study was compared with reported IDL values (Table 2). The value in this study was one order of magnitude lower than those obtained by others using bench top GC-EI-Sector-MS [14], LC-LIT-MS [18] and LC-triple quadrupole-MS [20], and were close to the levels obtained using GC-ECNI-MS [15,28] and GC-ICP-MS [19]. Although there is no information on IDL for GC-EI-Sector-MS, it was reported that its sensitivity is the same as that of GC-ECNI-MS [15,28] and GC-ICP-MS [19]. Although the sensitivity of this method was 10 times lower than that of GC-ECNI-MS [16], this method was more selective. Thus, sensitive quantification was achieved using conventional GC-EI-qMS under modified conditions. Recoveries of the analytes through this method were evaluated by comparison of clean up spike to syringe spike ratios in sample extract with those in standard solution. The recoveries in sediment, house dust and mussel samples were 80-95, 85-105 and 60-80% for $^{13}C_{12}$-BDE-197, -207 and -209, respectively (Table 1).

3.3 *Validation of the method*

In order to evaluate the reliability of the method, we analysed certified reference materials and samples which were analysed before. Descriptions of the samples and results of comparison are listed in Table 3.

Analysis of the SRM2585 reference dust samples showed that our BDE-209 result (2703 ± 140 ng/g dry wt) was in good agreement with the certificated value (reported value; BDE-209, 2510 ± 190 ng/g dry wt) [29]. Although, our BDE-206 (nona-BDE) result (188 ± 14 ng/g dry wt) was somewhat lower than the certificated value (reported value;

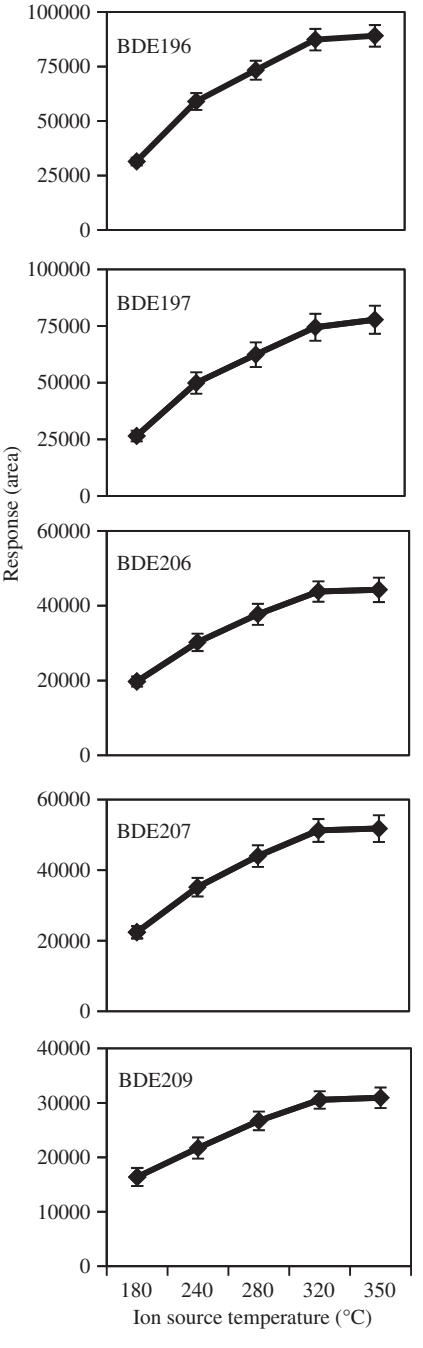

Figure 1. Abundance of individual PBDE congeners when the temperature of the ion source of the mass spectrometer was set at 180, 240, 280, 320 and 350°C.

Table 2. Comparison of instrumental detection limit (IDL) for BDE-209 (pg).

Instrument	Separation	Ionisation type	Analyser	IDL (pg)	Reference
Agilent 5975C	GC	EI	Quadrupole	0.6	This study
JEOL GC-Mate II	GC	EI	Sector (Bench top)	3	[14]
Shimadzu GCMS-QP2010	GC	EI	Quadrupole	0.8	[28]
Shimadzu GCMS-QP2010	GC	PCI	Quadrupole	9.7	[28]
Shimadzu GCMS-QP2010	GC	ECNI	Quadrupole	0.4	[28]
HP 5973C	GC	ECNI	Quadrupole	0.06	[16]
Agilent 5973	GC	ECNI	Quadrupole	0.87	[15]
API 3200Q	LC	APPI	Triple Quadrupole	28	[20]
LCQ Deca XP	LC	APPI	Linear ion trap	1500	[18]
HP 4500	GC	ICP	Quadrupole	0.1	[17]

Table 3. Comparison of the consensus values from the inter-laboratory exercise with the values for BDE-209 concentrations in mussels (ng/g lipid wt) between GC-EI-qMS and Bench top GC-EI-Sector-MS [14].

Location	Previous method [14]	GC-EI-qMS
India, Pondicherry (2004)	<2.0	<0.5
China, Qingzhou (2004)	<2.0	4.1
Hong Kong, Tsim sha Tsui (2004)	13	12
China, Dalian (2004)	30	36
China, Beihai (2004)	2.8	4.7
China, Lian Yung Gang (2004)	7.7	9.7

Previous Method: GC-EI-Sector-MS: GC-Mate II used in the previous report [14].

GC-EI-qMS: Agilent 7980A GC equipped with Agilent 5975C MS used in the present study.

BDE-206, 271 ± 42 ng/g dry wt), the present method seems to be reliable since the recoveries of clean up spike were high (75–110%) and the variation of the values were relatively low (RSD = 7%) [29]. Taking into account that BDE-209 is approximately one order more abundant than BDE-206 in SRM2585, these results suggest that the degradation of BDE-209 as well as the formation of nona-BDE as degradation product were negligible.

The sediment sample which was used for an inter-laboratory calibration exercise (NIES CRM Air Dried Sediment#1) was also analysed [23]. The inter-laboratory calibration exercise using NIES CRM Air Dried Sediment#1 was carried out among eight research institutions and the reported concentration in 146 ± 16 ng/g dry wt for BDE-209. Concentration of BDE-209 using the present method was 153 ± 2.3 ng/g dry wt ($n = 5$), whereas it was 151 ± 17 ng/g dry wt ($n = 5$) using our previous method [14]. Both the values were in the range of reported values (140–170 ng/g), indicating that the present method also gives reliable data for sediment analysis. When compared to our previous method, RSD has improved from 15.7% (previous method) to 3.4% in the present method. Furthermore, mussel samples, for which the concentrations of PBDEs were reported in our previous study, were also analysed for comparison [14]. The concentrations determined using the present method were in agreement with the reported values (Table 3).

Differences were approximately 20% or less for samples with high concentration. However, the difference was larger with concentration close to detection limit of the previous method. The analytical method developed in the present study with modified MS conditions can be applied to various environmental matrices and would provide sensitive and reliable analytical results. An inter-laboratory calibration exercise for higher brominated PBDEs is warranted since only a limited number of certified values are available so far.

4. Conclusions

A sensitive, selective, simple and robust analytical method for the analysis of higher brominated PBDEs using GC-EI-qMS and isotope dilution was developed. Peak area of BDE-209 at 320°C or higher was about 2 times higher than that at 180 and 240°C, indicating that the sensitivity is greater at the higher ion source temperatures. The IDLs was 0.6 pg for BDE-209. It was found that the sensitivity of GC-EI-qMS was similar to GC-ECNI-MS and GC-ICP-MS. Validation of the method was carried out by analysis of house dust (NIST SRM2585), sediment (NIES CRM Air Dried Sediment#1) and mussel samples. The method developed in the present study is applicable to various environmental matrices. The biggest advantage of this method is that higher brominated congeners of PBDEs can be determined using conventional GC-EI-qMS.

Acknowledgements

This study was supported by Global COE Program and Grants-in-Aid for Scientific Research (S: 20221003, Young Scientists B: 19780239) of the Ministry of Education, Culture, Sports, Science and Technology, Japan (MEXT) and Japan Society for the Promotion of Science (JSPS). This research was partly supported by MEXT's program 'Promotion of Environmental Improvement for Independence of Young Researchers' under the Special Coordination Funds for Promoting Science and Technology.

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