ESTABLISHMENT OF AN ANALYTICAL METHOD FOR DETECTING DECABROMODIPHENYL ETHER AND EVALUATION OF ITS THERMAL DECOMPOSITION PRODUCTS

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Introduction

Decabromodiphenyl ether (BDE-209) is used as a brominated flame retardant, and the total production and amount imported into Japan were approximately 1,100 tons in fiscal year 2014[1]. BDE-209 has been reported to have toxic effects and was added to Annex A (elimination) at the eighth Conference of the Parties of the Stockholm Convention on persistent organic pollutants (POPs) (Geneva, April 24 to May 5, 2017)[2].

As a current constituent of certain existing products, BDE-209 must be decomposed to reduce its concentrations until the products can be classified as having a low POP content[3]. Decomposition targets were set in the Basel Convention on hazardous wastes, with destruction efficiency (DE) and destruction removal efficiency (DRE) values of 99.999% and 99.9999%, respectively[4]. A DE >99.999% and DRE >99.999% are "decomposing targets in the Basel Guidelines". Several cases of thermal decomposition tests for BDE-209 have been reported previously[5~9].

In this study, we established an analytical method for detecting BDE-209 using gas chromatography–mass spectrometry (GC-MS) and conducted a thermal decomposition test to evaluate the thermal decomposition technique, including the resulting decomposition byproducts. We assessed the method used to measure BDE-209 and analyzed the thermal decomposition products qualitatively and quantitatively using the established analytical method.

Materials and methods

Materials: BDE-209 was obtained from Wako Pure Chemical Industries, Ltd (Kyoto, Japan) as a white or gray powder (purity 98%). The chemical formula and molecular weight of BDE-209 are $(C_6Br_5)_2O$ and 959.17, respectively. The powder was stored in an opaque bottle in the dark at 25℃ or lower. A standard sample of BDE-209 solution in toluene (50 ± 2.5 μg/mL, chemical purity > 98%; Wellington Laboratories), an internal standard sample of $^{13}C_{12}$-BDE-209 solution in toluene (25 ± 1.2 μg/mL, chemical purity >98%, isotopic purity 99.99%) and an internal standard sample of $^{13}C_{12}$-BDE-206 solution in toluene (50 ± 2.5 μg/mL, chemical purity >98%, isotopic purity 99.99%) were stored in an opaque bottle at 5℃.

Analytical method for BDE-209 : The measurements were performed under the following conditions. A qualitative analysis of the BDE-209 powder was conducted by the selection of measurement column, determining the optimum concentration for injection, and quantitating error via repeated measurements. Qualitative analyses of $^{13}C_{12}$-BDE-209,$^{13}C_{12}$-BDE-206, and the BDE-209 standard sample were also conducted by creating a calibration curve and measuring the lower limit of quantification. The analytical method was then established[10].

Thermal decomposition test : Using a high-temperature tube furnace, we heated 1.0 g BDE-209 powder for 60 min (**Figure 1**). We used temperatures of 400 and 850℃, synthetic air as the measurement gas, and a flow rate of 200 mL/min. The incinerators currently used to dispose of waste containing low concentrations of the

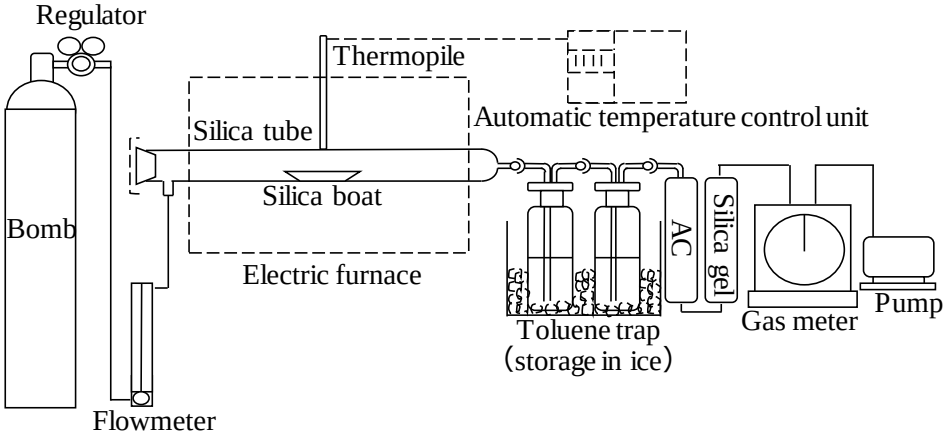

Figure1：Structure of the tube furnace

polychlorinated biphenyls require a temperature of 850℃ or higher with a residence time of 2s or longer. The selection of our conditions for the thermal decomposition test was also based on the results of a thermogravimetric analysis. Three types of sample were used for the measurements: (1) the encrustation in the silica tube and glass wool of the silica tube exit, (2) the residue on the silica boat, and (3) a toluene trap for the exhaust gas. We pretreated the samples for each measurement and introduced them into the GC-MS instrument (GCMS-QP2020/GC-EI-qMS Shimadzu Corporation, Kyoto, Japan). Quantitative and qualitative analyses were conducted using the established analysis conditions. For the thermal decomposition test, we calculated DE and DRE values at each temperature by quantitative analysis. The internal standard sample was detected only in the residue sample of the thermal decomposition test conducted at 850℃, and therefore we calculated the value of DE and DRE using an internal standard method. The internal standard sample was not detected in the samples, except for the residue sample of the 850℃ thermal decomposition test, and therefore we calculated the value of DE and DRE using an absolute calibration curve. In addition, we evaluated the resolution of the byproducts of each sample by qualitative analysis. We performed a similarity search for each peak detected on the chromatogram to identify the organic compounds.

Results and discussion:

We established a GC-MS analytical method in this study. For the measurement column, we used an Ultra Alloy-1 (MS/HT) column due to its measurement efficiency. We determined the optimum sample concentration for injection as 0.1–100 µg/mL. We corrected the variation in the peak area value based on the internal standard sample via quantitation of the error by repeated measurements. After establishment of the measurement method, we performed the method in the commonly used scan and SIM analysis modes. The fixed-quantity lower limit level was 0.112 µg/mL (**Table 1**).

Table 1: Established gas chromatograph mass spectrometry (GC-MS) analytical method

The selection of measurement column	Ultra Alloy-1 (MS/HT)
The optimum sample concentration for injection	0.1~100 µg/mL
The calculation method of concentration by calibration curve	Internal standard method (※Absolute calibration method)
Measurement method (SCAN mode)	Retention time = 3.00min ~ 20.00min, Range of m/z = 100.00 ~ 1000.00
Mesurement method (SIM mode)	Retention time = 3.00min ~ 20.00min, ch1 = m/z 799.40, ch2 = m/z 801.40, ch3 = m/z 797.40, ch4 = m/z 811.40, ch5 = m/z 809.40, ch6 = m/z 813.40, ch7 = m/z 731.55, ch8 = m/z 733.55, ch9 = m/z 735.55
The fixed-quantity lower limit level	0.112 µg/mL

The mass values in each sample indicated that the tube encrustation and glass wool sample contained the highest levels of BDE-209. In the 850℃ thermal decomposition sample, the concentration of BDE-209 was high in the encrustation in the silica tube and glass wool samples. The concentration was lower in each of the residues the encrustation in the silica tube, glass wool, and toluene trap in the 850℃ thermal decomposition sample than in the

Table2 : Mass of BDE-209 of each sample in 400℃ and 850℃ thermal decomposition test, and a value of DE and DRE

400℃ thermal decomposition test	
Mass of BDE-209 in the residue(g) (= C_{r1})	8.4×10^{-5}
Mass of BDE-209 in the jurisdiction encrustation and glass wool (g) (= C_{r2})	3.4×10^{-2}
Mass of BDE-209 in the toluene trap(g) (= C_g)	1.5×10^{-6}
Mass of BDE-209 in the all themal decomposition products (g) (= C_{All})	3.4×10^{-2}
Theoretical mass of BDE-209 in the samples before the thermal decomposition (g) (= C_{waste})	0.98
DE (%) (= $(C_{waste} - C_{All}) / C_{waste}$)	96.5437
DRE (%) (= $(C_{waste} - C_g) / C_{waste}$)	99.99984

850℃ thermal decomposition test	
Mass of BDE-209 in the residue(g) (= C_{r1})	2.2×10^{-7}
Mass of BDE-209 in the jurisdiction encrustation and glass wool (g) (= C_{r2})	7.6×10^{-6}
Mass of BDE-209 in the toluene trap(g) (= C_g)	6.1×10^{-7}
Mass of BDE-209 in the all themal decomposition products (g) (= C_{All})	8.5×10^{-6}
Theoretical mass of BDE-209 in the samples before the thermal decomposition (g) (= C_{waste})	0.98
DE (%) (= $(C_{waste} - C_{All}) / C_{waste}$)	99.9991
DRE (%) (= $(C_{waste} - C_g) / C_{waste}$)	99.99994

400℃ thermal decomposition sample. And more BDE-209 remained in the encrustation in the silica tube and glass wool in the each temperature sample. This was believed to be due to the non-uniform temperature in the tube furnace.

The DE and DRE values were 96.5437% and 99.99984%, respectively, in the thermal decomposition test performed at 400℃ compared with 99.9991% and 99.99994%, respectively, in that performed at 850℃ (**Table 2**). We can therefore conclude that when BDE-209 is decomposed thermally at 850℃, a DE value of >99.999% and DRE value of >99.9999%, as defined in the Basel Convention guidelines, can be achieved. Using the absolute calibration method instead of the internal standard method for the residue sample from the 850℃ thermal decomposition test, the mass of BDE-209 in the residue sample was determined to be 9.90×10^{-8} g. Accordingly, the DE value was 99.99915%, and the change in the DE value determined using the BDE-209 mass calculation method in this test was very small. Regarding the thermal decomposition tests, we plan to derive decomposition rate equations based on temperature and residence time in future studies. Because the internal standard sample, $^{13}C_{12}$-BDE-209 (cleanup spike), was not detected, the extract obtained by Soxhlet extraction was separated, and the internal standard sample $^{13}C_{12}$-BDE-209 was added to the separated extract. Use of an internal standard is necessary to enable quantification.

Among the decomposition byproducts, polybrominated diphenyl ethers (PBDEs) such as octa-BDE, nona-BDE, and BDE-209 were particularly abundant in tube encrustations and residues of the 400℃ thermal decomposition samples, whereas bromine-based organic compounds other than PBDEs, including hexabromobenzene, octabromodibenzofuran (octa-BDF), 2,7,9-tribromofluorene, and 1,5-dibromo-2,6-bis(bromomethyl)-naphthalene, were present in all of the thermal decomposition samples. These results can be supported by the following research. In a previous study[8] of thermal decomposition tests conducted on polystyrene containing BDE-209, polybrominated dibenzo-p-dioxins and dibenzofurans, brominated biphenyls, PBDEs, and brominated benzenes were identified in the exhaust gas and residues. Hexabromobenzene is produced readily and abundantly during thermal decomposition of BDE-209 upon splitting of the ether bond of BDE-209, which results in a bromine-bound fragment. The peaks observed at the retention times of 17.2–17.4 min (**Figures 2A, 2D**) were identified as BE-209 by a similarity search. Although a peak representing BDE-209 was not expected at this retention time, the

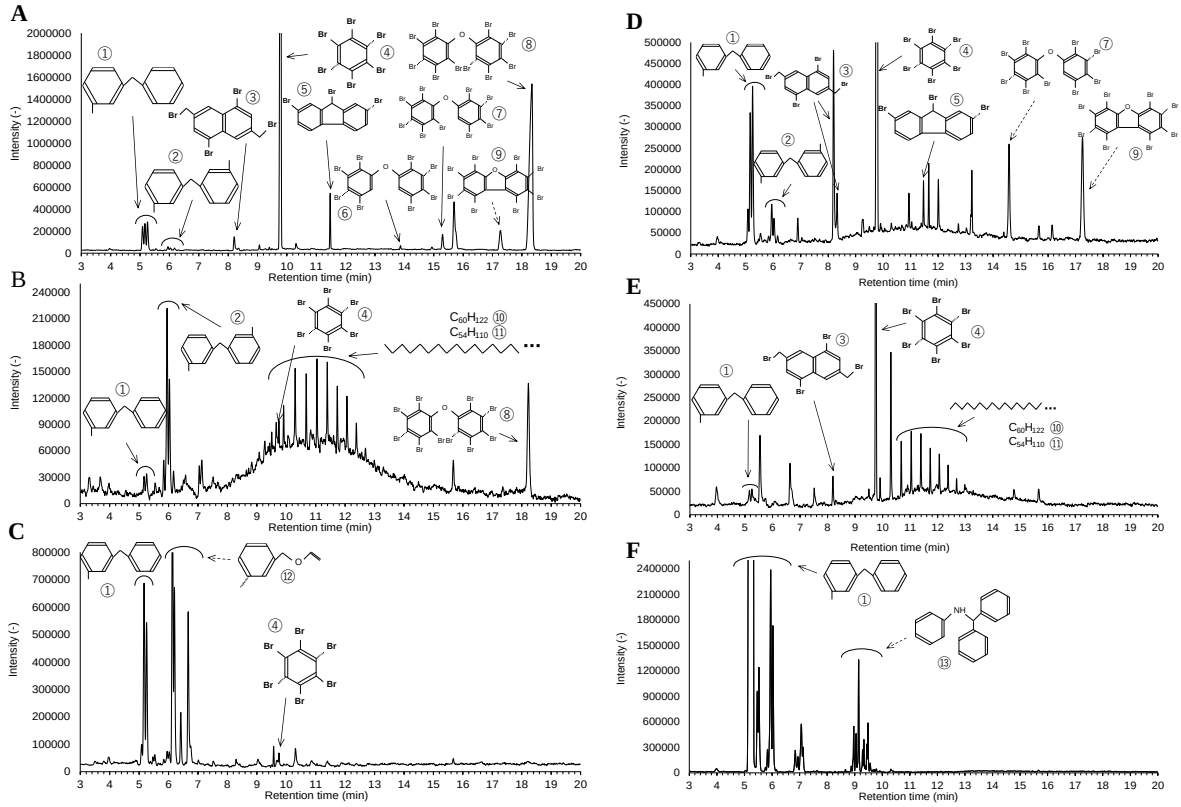

Figure 2: Evaluation of chromatograms and byproducts of each 400℃ and 850℃ thermal decomposition sample. (A): The 400℃ sample tube encrustation at 100-fold dilution, (B): 400℃ sample residue at 100-fold dilution, (C) 400℃ sample toluene trap at 10-fold dilution, (D) 850℃ sample tube encrustation at 100-fold dilution, (E) 850℃ sample residue undiluted, (F) 850℃ sample toluene trap at 500-fold dilution. ① 1-methyl-2-phenylmethyl-benzene, ② 1,1'-methylenebis [2-methyl-benzene], ③ 1,5 dibromo-2,6-bis(bromomethyl)-naphthalene, ④ hexabromobenzene, ⑤ 2,7,9-tribromofluorene, ⑥ octa-bromodiphenyl ether, ⑦ nona-bromodiphenyl ether, ⑧ BDE-209, ⑨ octa-bromodibenzofuran, ⑩ hexacontane, ⑪ tetrapentacontane, ⑫ p-methylbenzylvinylether, ⑬ N-[(2-methylphenyl)(phenyl)methyl]benzenamine.

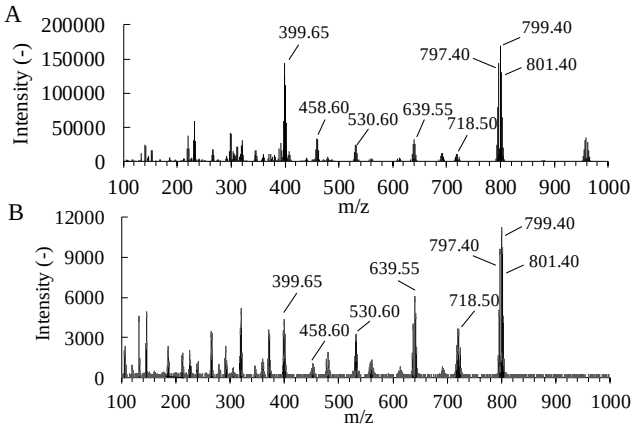

Figure 3： Comparison of the mass chromatograms of BDE-209 (A) and octa-BDF (B).

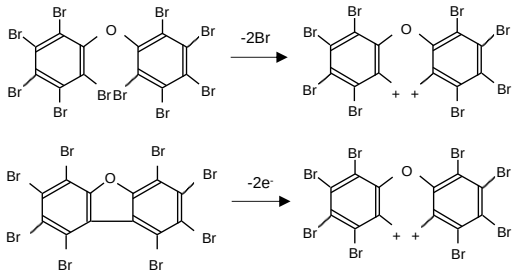

Figure 4： Cleavage of BDE-209 and octa-BDF

cleavage pattern on the mass chromatogram was very similar to that of BDE-209 (**Figure 3**). This is most likely due to the complete coincidence between a fragment ion in which two bromines have cleaved from BDE-209 and the daughter ion of octa-BDF (**Figure 4**)[11]. Therefore, the peak at the retention time of 17.2–17.4 min is likely octa-BDF. Long-chain alkanes in the residue sample and low-molecular-weight compounds containing a benzene ring in the toluene trap were clearly observed at 400℃ and 850℃. A large number of peaks representing compounds lacking bromine with two bound benzene rings was confirmed at a retention time of 5–6 min in all samples (**Figure 2**). Some of these decomposition byproducts were toxic and will require further study.

Conclusion:

BDE-209 is used as a brominated flame retardant and has been reported to have adverse health effects. It was added to Annex A (elimination) at the eighth Conference of the Parties of the Stockholm Convention on POPs. The DE and DRE were defined as decomposition targets in the Basel Convention, with target values of 99.999% and 99.9999%, respectively. Despite this, there have been few studies on the thermal decomposition treatment of BDE-209.

The DE and DRE values were 96.5437% and 99.99984%, respectively, in the 400℃ thermal decomposition test compared with 99.9991% and 99.99994%, respectively, in the 850℃ thermal decomposition test. Therefore, when BDE-209 is decomposed at 850℃, a DE of >99.999% and DRE of >99.9999%, as defined in the Basel Convention guidelines, can be achieved. However, in the qualitative analysis, harmful PBDEs and brominated organic compounds were identified as decomposition byproducts. Some PBDEs, hexabromobenzene, and octa-BDF are classified as toxic and thus will require further studies of their formation.

Acknowledgements:

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