Purity Evaluation of Tetrabromobisphenol-A by Differential Scanning Calorimetry

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Introduction

Brominated flame retardants (BFRs), which are environmentally persistent and potentially toxic, have been produced since the 1970s in several countries, and they are used to reduce inherent fire hazards in a variety of consumer goods (de Wit 2002). Among BFRs, tetrabromobisphenol-A (TBBPA) is produced in the USA and Japan (European Committee 2007), and was reported as a BFR with the highest production volume, covering over 50 % of the total BFR market (Law *et al*. 2006). TBBPA is covalently bound to plastic, and is used in electronic circuit boards (de Wit 2002). Industrial use of TBBPA is not restricted now, though brominated biphenyls and -diphenyl ethers are banned to be contained in electrical and electronic equipments put on the market in the RoHS regulation provisions. However possibility of thyroid hormone and estrogen activities on TBBPA was reported (Kitamura *et al*. 2002), and moreover it was suggested that combustion of consumer goods containing TBBPA may lead to formation of another class of highly toxic compounds such as brominated dibenzo-*p*-dioxins and -dibenzofurans (Wichmann *et al*. 2002). Furthermore several investigations were also conducted to clarify concentration of TBBPA in the environment (Morris *et al*. 2004, Suzuki and Hasegawa 2006), and therefore use of certified reference materials (CRMs) for the calibration and standardization is essentially important for accurate determination of TBBPA.

In certification of organic CRMs, freezing point depression method using a differential scanning calorimeter (DSC) is effective for reliable purity evaluation (Shimizu *et al*. 2008, Hanari *et al*. 2009). This method is regarded as one of the primary methods of measurement, because analytical value obtained by this method is potentially traceable to the International System of Units (SI) (Milton and Quinn 2001). In this study, we applied DSC for purity evaluation of TBBPA. Moreover, amount of TBBPA in Firemaster BP-4 which has been widely used as commercial preparations (Brown *et al*. 2004) was quantified using a TBBPA calibrant which purity was evaluated by DSC measurement.

Materials and Methods

TBBPA (lot 006X1577) for environmental analysis was obtained from the Kanto Chemical (Tokyo, Japan). Standard Reference Materials (SRMs) 2225 (Hg) and 2232 (In) used as calibration standards (temperature and enthalpy of fusions) for DSC measurement were purchased from the National

Institute of Standard and Technology (NIST; Gaithersburg, MD, USA). Bisphenol-A (BPA; NMIJ CRM 4030-a) was used as an internal standard (IS) for quantification of TBBPA in Firemaster BP-4 (lot FR-006-A, AccuStandard, New Haven, CT, USA). DSC measurement of TBBPA was carried out using a DSC 822e (Mettler Toledo, Schwerzenbach, Switzerland). TBBPA (2.2 – 3.8 mg) was sealed into a 40-µL aluminum crucible under a dried-nitrogen atmosphere. To confirm that TBBPA had not been lost during the DSC measurement, the crucible was weighted on completion of the measurement. After calibration using SRMs, melting point and enthalpy of fusion on TBBPA could be analyzed with a continuous scan method at a heating rate of 0.1 °C min^{-1}. Purity of TBBPA was determined from fractional melting in accordance with the method given in the literature (van Dooren and Muller 1984). A Shimadzu 2010 GC-FID system (Kyoto, Japan) was used for quantification of residual solvent. Column oven temperature was programmed from 150 °C (7 min) to 300 °C at a rate of 60 °C min^{-1}, with a final hold time of 50 min. A column used was DB-5 (60 m × 0.32-mm i.d., film thickness 1.0 µm, J&W Scientific, Folsom, CA, USA). Injector and detector temperatures were held at both 300 °C. Moisture in TBBPA was evaluated by using an AQ-7 Karl-Fischer moisture content meter equipped with a coulometric titration system (Hiranuma Sangyo, Mito, Japan) at room temperature under a dried-air atmosphere. Sample was measured in replicates as possible after validation using a standard solution of water.

We gravimetrically prepared measurand and calibration solutions with neat reagents and acetone for pesticide residual and PCB analysis (Wako Pure Chemical Industries, Osaka, Japan). TBBPA which purity was evaluated was used as a calibrant in order to quantify amount of TBBPA in Firemaster BP-4. A model HPLC 1100 series (Agilent Technologies, Palo Alto, CA, USA) equipped with a diode-array detector was operated with 85 % methanol–water. A L-column ODS (250 mm × 4.6 mm i.d., Chemicals Evaluation and Research Institute, Tokyo, Japan) was used at a flow rate of 1.0 mL min^{-1} and an oven temperature of 40 °C. Chromatographic data were obtained by monitoring the absorbance at wavelengths 210, 254, and 280 nm.

Results and Discussion

Purity of TBBPA based on DSC measurement was obtained as follows. The van’t Hoff plots (van Dooren and Muller 1984) were constructed from DSC data and then melting point of TBBPA was obtained. In addition, enthalpy of fusion was obtained from melting curve of TBBPA. Next, the mole fraction of impurity (mol/mol) was calculated by the van't Hoff equation using the above results and the literature data (Coplen and Peiser 1998, Mohr and Taylor 1999). Furthermore volatile impurities (residual solvent and moisture) were independently measured by using GC-FID and Karl-Fischer moisture content analyses. Because melting point of this TBBPA was 182 °C, volatile impurities

evaporated from TBBPA before melting. Thus, purity of TBBPA was calculated by subtracting the mole fraction of impurity from 1, and was determined with 0.9986 (mol/mol). Uncertainty of purity evaluation was estimated based on the GUM (ISO 1993). From the data calculated in this study, the uncertainty was estimated with 0.0004 (mol/mol), and then it was indicated that one of the main sources of uncertainty came from variation of analytical results of TBBPA. Validation of the purity was accomplished by comparing impurity data from GC-FID, HPLC and Karl-Fischer moisture content analyses, and results of impurity (two main impurities were tribromobisphenol-A and moisture) allowed within uncertainty of purity evaluation based on DSC measurement.

On the other hand, no DSC measurement was applicable to Firemaster BP-4, because reliable purity evaluation using DSC required highly pure compounds (> 98 % mol/mol) (van Dooren and Muller 1984). For quantification of TBBPA in Firemaster BP-4, measurand solution (Firemaster BP-4 with BPA) and calibration solution (TBBPA with BPA) were analyzed using bracketing injections (Figure 1). Masses of each neat reagent of prepared solutions were 0.849 mg (Firemaster BP-4; analyte), 3.81 mg (TBBPA; calibrant) and 14.6 mg (BPA; IS), respectively. Peak area of BPA of each solution was standardized based on the prepared concentration, and then standardized peak areas were used for quantification. Moreover purity of TBBPA of the mole fraction was converted into that of the mass fraction (kg/kg) based on the result of average molecular weight of impurities of TBBPA used. From the result obtained in this study, amount of TBBPA in Firemaster BP-4 was determined with (94.7 ± 1.9) % of the mass fraction. Uncertainty of quantification was estimated as well as purity evaluation, and two of the main sources of the uncertainty came from variation of analytical results and from uncertainty of balance used.

Thus, reliable purity evaluation of TBBPA based on DSC measurement and accurate quantification of TBBPA in Firemaster BP-4 using the purity evaluated TBBPA were achieved. Furthermore, accurate quantification of TBBPA in the environment seems to be fulfilled by using this TBBPA.

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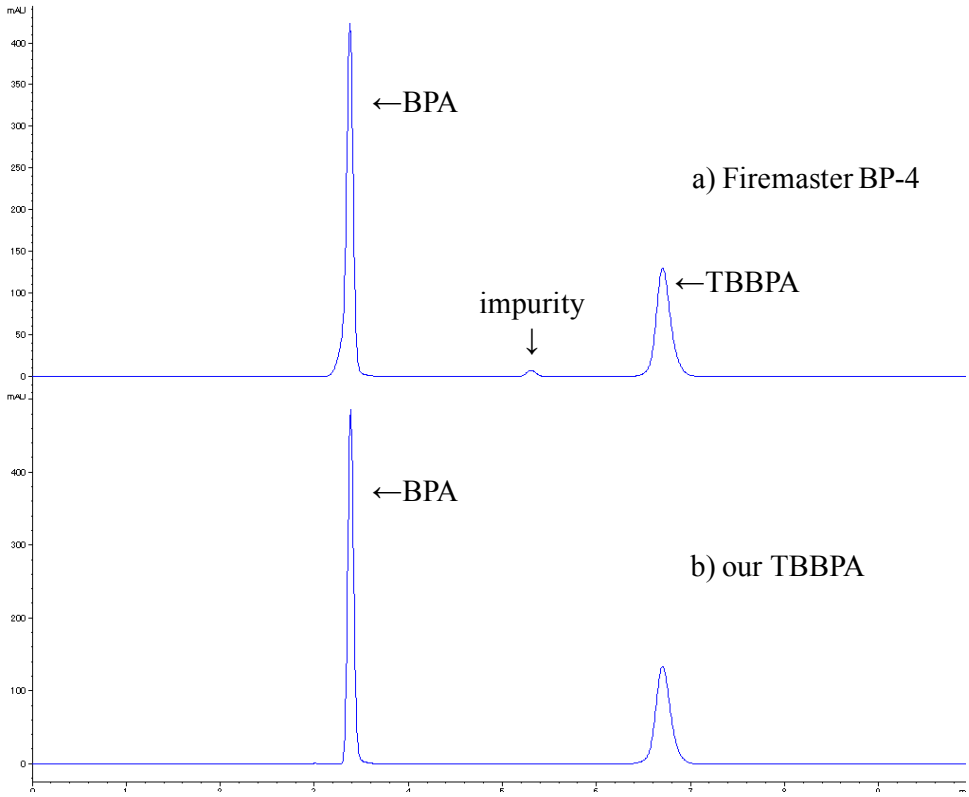

Figure 1; LC chromatograms (λ: 280 nm) on quantification of TBBPA in Firemaster BP-4.
a) Firemaster BP-4 with BPA, b) TBBPA with BPA, BPA: Internal Standard.