PREPARATION OF QUALITY CONTROL PLASTIC SAMPLES INCLUDING ORGANOCHLORINE, ORGANOBROMINE, ORGANOPHOSPHORUS, AND ANTIMONY AS FLAME RETARDANTS

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Introduction

Flame retardants (FRs), which are chemicals added to materials both to prevent combustion and to delay the spread of fire after ignition, are used in polymers since the 1960s[1-3]. FRs may contain halogens (chlorine and bromine), phosphorus, aluminum, and magnesium, or antimony trioxide, etc.[2]. Particularly, organochlorine, organobromine, and organophosphorus FRs, which are major groups of organic FRs[3], have been widely used in commercial plastics such as electric and electronic products. Recently, usage of antimony trioxide has increased constantly because this compound is generally used to enhance halogen flame retardant efficiency[4]. However, it was concerned that the plastics were recognized as contamination sources in the environment because the plastics contain a few percent of FRs. Besides, release of FRs from the plastics could not be managed throughout these supply chain. Under such situation on FRs, it is desired to accurately manage behaviors of FRs contained in the plastics. For accurate managements of the behaviors, reliable analytical results are needed.

In these days, we can use matrix reference materials including additives to validate analytical results obtained using well-known methods (and/or new methods). However, these reference materials were specified for managements of RoHS (e.g. PBDEs), REACH (e.g. phthalates), etc.[5,6], therefore, it is difficult to apply to proper managements of the plastics including FRs such as organochlorine, organobromine, and organophosphorus throughout these supply chain. Additionally, a relationship between organic and inorganic FRs have not been known well. In this study, to satisfy these requirements, we prepared quality control (QC) samples including appropriate FRs with sufficient preparation concentrations as plastic disks. After preparing, the capability (homogeneity, stability, and characterization) of prepared disks was evaluated using analytical results obtained by GC/MS for dechlorane plus (DP), tetrabromobisphenol A (TBBPA), and triphenyl phosphate (TPhP) in either acrylonitrile-butadiene-styrene (ABS) or polycarbonate (PC). The further capability of these disks was also evaluated using the results obtained by energy dispersive X-ray fluorescence (ED-XRF) spectrometry for Cl, Br, P, and antimony trioxide (Sb).

Materials and methods

Raw materials of QC samples were commercial ABS resin (Nippon A&L, Japan) or PC resin (Mitsubishi Engineering Plastics, Japan). DP (OxyChem, USA), TBBPA (Tokyo Chemical Industry, Japan), TPhP (Tokyo Chemical Industry), and Sb (Wako Pure Chemical Industries, Japan) were used for FRs. Tetrahydrofuran (THF) was purchased from Kanto Chemical (Japan) and *n*-hexane and toluene were purchased from Wako Pure Chemical Industries. DP, TBBPA, TPhP, PCB 170 (CIL, USA), and PCB 180 (AccuStandard, USA) were prepared in toluene using gravimetric preparation method[7]. For organic FRs, an Agilent Technologies (USA) 6890 GC equipped with a DB-17MS column (15 m × 0.25 mm i.d., 0.15 μm film thickness; Agilent Technologies), and a 5975B MSD was used for homogeneity/stability tests and characterization. Analysis was performed by using on–column injection mode, and injection volume was 0.5 μL. Helium was used as the carrier gas (1.0 mL/min) and inlet temperature was set as oven track mode. Organic FRs were monitored with EI ionization and SIM mode. Column oven temperature was programmed from 50 °C (2 min) to 300 °C at a rate of 20 °C/min with a final hold time of 15 min. DP, TBBPA, and TPhP were quantified by internal standard method, and PCB 170 was used as the internal standard. DP was quantified as the sum of the peak area for syn- and anti-DP. For elemental analysis, a Shimadzu XRF Rayny EDX-720 (Japan) was used for homogeneity test. Operating conditions of ED-XRF spectrometer for Cl (Kα), Br (Kα), P (Kα), and Sb (Lα) are as follows; X-ray irradiation from lower side of sample, Rh target (air cooling), tube voltage 15 kV, tube current 800 μA, Al filter, vacuumed sample chamber, X-ray irradiated diameter to sample 10 mm, measurement time 9999 sec.

Homogenization of QC samples was evaluated based on quantitative values obtained with GC/MS for organic FRs and based on X-ray intensities obtained with ED-XRF spectrometer for elements. For organic FRs, the

between-bottle (disk) homogeneity was estimated by determining the values in two sub-samples that were taken from 10 randomly selected from the total disks in each. Additionally, for the elements, the between-disk homogeneity was also estimated by determining the intensities in 14 for ABS or 13 for PC disks randomly selected from the total. Estimation of homogeneity was evaluated by analysis of variance (ANOVA) described in the publication[8]. Additionally, the mean squares among-group (MS_{among}) and within-group (MS_{within}) were calculated, then, the standard deviations between the disks (s_{bb}) and the influences of the analytical variations on the standard deviations between units (u_{bb}) were estimated from the data.

Results and discussion

Preparation of QC samples. QC samples were prepared by mixing commercial ABS or PC (confirmed to have no target FRs detectable in both) resin powder, DP, TBBPA, TPhP, and Sb. The mixing to homogenization on ABS or PC resin was respectively carried out by a kneading machine for a total of two times. Each mixed material was injection-molded with an injection molding machine; then, the injection-molded plates were cut as disks (approximately 1000 ABS and 800 PC disks). These form is a disk with a diameter of 30 mm, a thickness of 2 mm, and a mass of 1.5 g. Each ABS or PC disk was made with target FRs to be DP and Sb: 500 mg/kg; TBBPA and TPhP: 1000 mg/kg.

Evaluation of homogeneity. For organic FRs, ABS or PC disk was respectively freeze-pulverized with a CryoMill (Verder Scientific, Germany). Each pulverized sample (0.1 g) was weighed in a PP tube. After addition of PCB 170 as the surrogate solution, dissolution of the sample was performed with 10 mL THF for 60 min using an ultrasonication equipment, which this condition was validated in elsewhere[9]. Obtained solutions were cleaned-up by precipitation with *n*-hexane on ABS or PC disk, then, PCB 180 as the syringe spike solution was added to this cleaned-up solution. Analytical results (as relative values) calculated using averages are shown in Fig. 1. By evaluating with ANOVA, result of the variance of between-disk homogeneity was not significant at 0.05 (*p*-value), so these organic FRs were homogenous. The s_{bb} was larger than the u_{bb} (DP in ABS, TBBPA in PC), so the s_{bb} was taken as the uncertainty of the homogeneity. In case that the s_{bb} could not be calculated due to the fact that $MS_{between}$ is smaller than MS_{within}[8], the u_{bb} was taken as the uncertainty (TBBPA and TPhP in ABS, DP and TPhP in PC). Based on these results, the relative standard uncertainty of the homogeneity on ABS disk was calculated as 0.69 % for DP, 1.46 % for TBBPA, and 1.54 % for TPhP, respectively. The relative standard uncertainty on PC disk was also calculated as 1.06 % for DP, 2.72 % for TBBPA, and 1.52 % for TPhP, respectively. It seemed that homogeneity on ABS and PC disks was equivalent to that on reference materials[6].

For elements, ABS or PC disk was directly evaluated once the center of disk, respectively. Before testing, operating conditions of ED-XRF spectrometer for Cl, Br, P, Sb analysis were optimized because intensity of light element, P, was relatively low and relative standard deviation (RSD) arising from analysis on P was obviously poor (above 10 %). To solve the problem, Al filter and vacuumed sample chamber were applied to the ED-XRF analysis. As a result, the RSD was improved (below 5 %). Analytical results from the ED-XRF on elements are shown in Table 1.

Evaluation of stability. The between-period stability as the short-term (30 days) instability was estimated by two-stage ANOVA. For organic FRs, result of the variance of between-period stability was not significant at 0.05 (*p*-value), so these organic FRs were stable. In this study, this instability was not considered as an uncertainty of stability. Supplementally, stability of the QC samples on organic FRs and elements is going to be monitored at regular intervals.

Characterization. Quantitative results obtained with GC/MS on organic FRs are shown in Table 2. The mass fractions of organic FRs were evaluated as mean values of analytical results. From the results in this study, RSDs arising from the data of DP, TBBPA, and TPhP obtained with GC/MS in ABS disk were calculated as 1.27 %, 2.85 %, and 2.76 %, respectively. The RSDs arising from those in PC disk were calculated as 2.41 %, 4.55 %, and 2.99, respectively. For accuracy of quantifications, RSDs of DP in both disks were better than those of others due to its physiochemical property. Moreover, standard deviation arising from quantification based on GC/MS analysis and uncertainty based on the homogeneity test were combined as the standard uncertainty (Table 2).

Eventually, our QC plastic samples were prepared properly, and they are useful tools for confirming the validity of analytical methods or instruments during quantification. Furthermore, these plastic disks are applicable to

elucidate behaviors of FRs throughout the supply chain and a relationship between organochlorine/ organobromine and antimony trioxide. Based on the results mentioned above, we are planning the weathering test using our QC plastic samples to investigate decomposition/vaporization/elution of organic and inorganic FRs from the plastics.

Acknowledgements
This work was supported by the Environment Research and Technology Development Fund (3K133009) of the Ministry of the Environment, Japan. The preparation of the QC samples was partly performed by the DJK Corporation.

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Table 1 Data of X-ray intensities obtained with ED-XRF on quality control plastic samples

ABS (n = 14)	P-Kα	Cl-Kα	Br-Kα	Sb-Lα
Average (cps/μA)	0.00345	0.02786	0.28309	0.05258
Standard deviation (SD)	0.00007	0.00019	0.00234	0.00056
Relative SD (%)	1.89	0.68	0.83	1.07

PC (n = 13)	P-Kα	Cl-Kα	Br-Kα	Sb-Lα
Average (cps/μA)	0.00128	0.02415	0.31139	0.04102
Standard deviation (SD)	0.00006	0.00018	0.00284	0.00025
Relative SD (%)	4.32	0.75	0.91	0.62

Table 2 Summary (mg/kg) of quality control plastic samples on organic FRs

	Dechlorane Plus	Tetrabromobisphenol A	Triphenyl phosphate
ABS disk			
Value	449	910	1,012
Standard uncertainty	6	29	31
PC disk			
Value	451	925	1,023
Standard uncertainty	12	49	34

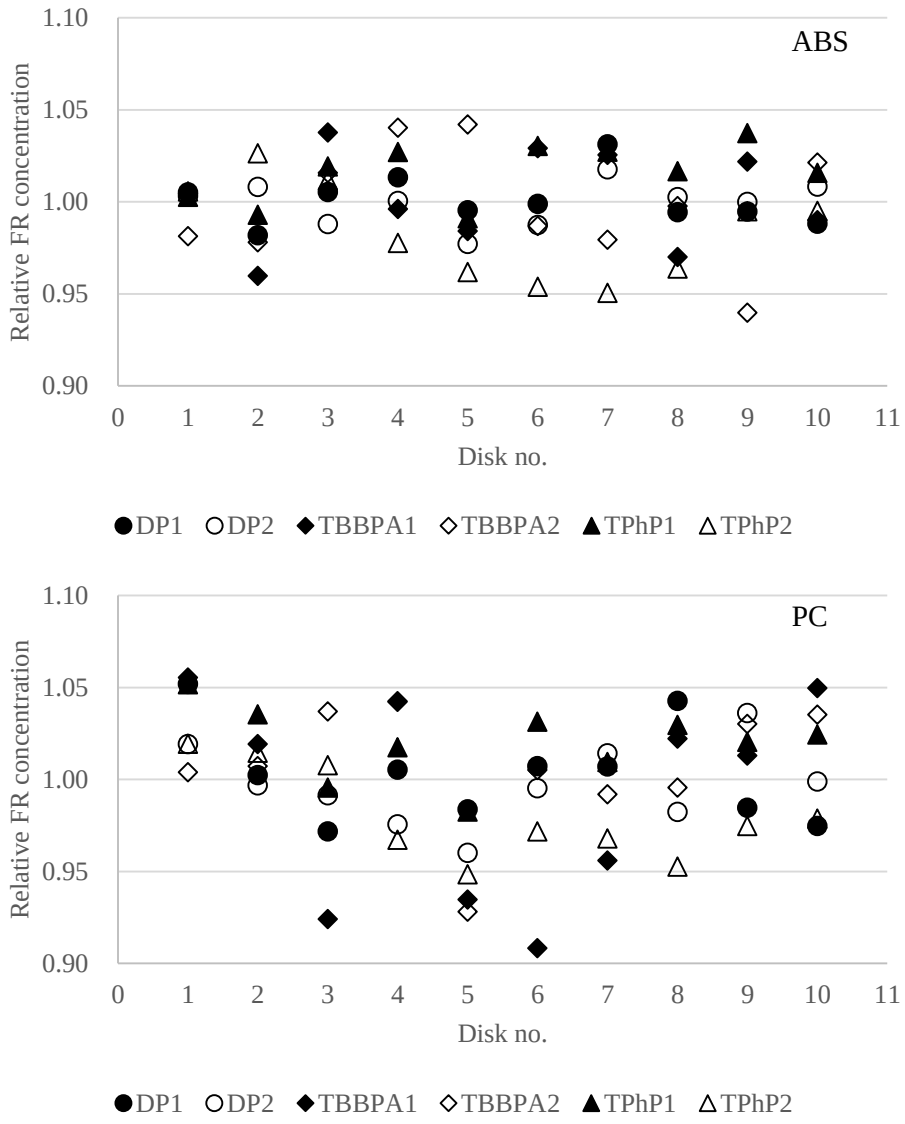

Fig. 1 Results of homogeneity test on ABS (upper) and PC (lower) disks for organic FRs