

EVALUATION OF MICROWAVE-ASSISTED EXTRACTION FOR THE ANALYSIS OF ORGANIC FLAME RETARDANTS IN ACRYLONITRILE-BUTADIENE-STYRENE

Otake T*, Itoh N, Ohata M, Hanari N

National Metrology Institute of Japan (NMIJ), National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1, Umezono, Tsukuba, Ibaraki 305-8563, Japan

Introduction

Flame retardants (FRs) are extensively used to prevent combustion and to delay the spread of fire after ignition¹. In particular, organochlorine, organobromine, and organophosphorus FRs (abbreviated as CFRs, BFRs, and PFRs, respectively), which are major groups of organic FRs², have been widely used in a commercial products such as acrylonitrile–butadiene–styrene (ABS) used for electric and electronic products (*e.g.*, televisions and computers). In terms of electronic waste management, the behaviors of organic FRs contained in ABS should be accurately evaluated. For accurate assessment of behaviors, accurate analytical results are essential.

Since the matrix of ABS is complicated, the pretreatment such as extraction is key operation to obtain the reliable analytical results. In ensuring reliability of the analytical results, the validation for method performance of FRs analysis is essential. Testing recovery by adding compounds (*e.g.*, surrogates) to matrix samples (“spiking”) is widely used and necessary for the evaluation of extraction techniques; however, this may be insufficient because there are solute–matrix interactions for native compounds. Even if the recovery yields of spiked compounds are satisfactory, native compounds may not be extracted adequately. Therefore, it is necessary to examine the extraction efficiency by using samples that contain the intended native compounds.

Ultrasonic extraction (UE) has widely employed for the extraction of organic FRs in plastics^{3,4}. As efficient alternatives, microwave-assisted extraction (MAE) has been introduced⁵. MAE enables batch process, can be automated, and needs only a small volume of solvent. However, as far as we know, no studies have evaluated MAE as the extraction technique of CFRs, BFRs, and PFRs in ABS. Further, the evaluation of MAE by using ABS sample containing target FRs has not been carried out. In this study, we optimized MAE parameters and evaluated the efficiency of MAE at extracting Dechlorane Plus (DP), tetrabromobisphenol A (TBBPA), and triphenylphosphate (TPhP) in ABS sample. The ABS samples were also analyzed by UE (used as reference technique) to compare with the results by MAE.

Materials and methods

Samples. ABS samples for the study of the optimization of MAE parameters were prepared so as to contain DP, TBBPA, and TPhP. A blank ABS (purchased from Nippon A&L; confirmed to have no target FRs detectable) was mixed with target FRs to be DP: 500 mg/kg; TBBPA and TPhP: 1000 mg/kg, then, ABS disks were produced (diameter: *ca.* 30 mm). These ABS disks were freeze-pulverized with a CryoMill (Verder Scientific, Germany), which were stored at below 10 °C under dark condition.

Extraction and clean-up procedures. *MAE.* ABS sample (0.1 g) was weighed in a glass extraction cell (GreenChem Plus; CEM, USA). After addition of the surrogate solution (PCB 170 in toluene), the sample was extracted with 10 mL tetrahydrofuran (THF) or toluene (Tol) for 10 or 20 min at 60, 90, or 120 °C in a microwave extraction system (MARSX, CEM) with power set at 100 % (1200 W). The extracts were cleaned-up by precipitation of the dissolved ABS matrix with hexane, then, syringe spike solution (PCB 180 in toluene) was added to this cleaned-up extract. *UE.* The sample was extracted with 10 mL THF for 60 min, which conditions were also validated although detailed data are not described here. The extract was cleaned-up as described for MAE.

Quantification by gas chromatograph with mass spectrometer (GC/MS). An Agilent Technologies (USA) 7890A GC equipped with a DB–5MS column (30 m × 0.25 mm *i.d.*, 0.25 μm film thickness; Agilent Technologies), and a 5975C MSD was used. The analysis was performed by using on–column injection mode, and the injection volume was 1.0 μL. A deactivated fused silica capillary (1 m × 0.25 mm *i.d.*; Agilent Technologies) was placed

as retention gap between the injector and DB-5MS column using a fused silica union to eliminate peak broadening of chromatogram. Helium was used as the carrier gas (1.0 mL/min) and the inlet temperature was set as oven track mode. The GC oven was programmed so that the temperature initially remained at 50 °C for 2 min, increased to 300 °C at a rate of 20 °C/min, and remained at 300 °C for 15 min. Quantitative analysis was conducted by SIM mode and m/z of the ions for quantification were as follows: DP, 271.8; TBBPA, 528.7; TPhP, 326.1; PCB 170 and 180, 393.8. DP, TBBPA, and TPhP were quantified by internal standard method, and PCB 170 was used as internal standard. DP was quantified as the sum of the peak area for *syn*- and *anti*-DP.

Results and discussion

Influence of MAE temperature and time. The extraction temperature and time are important factors for MAE⁶, therefore, these conditions were optimized. A high temperature decreases the viscosity of the extraction solvent and helps to disrupt solute–matrix interactions, thus enabling a higher extraction efficiency to be obtained⁶. On the other hand, an unnecessarily high temperature and long extraction time might also extract unwanted compounds and degrade the target compounds.

The effects of the extraction temperature are given in Fig. 1 ($n = 3$; THF was used as extraction solvent in this section). Observed concentrations will be biased if target compounds are not extracted adequately. Our results showed that observed concentrations obtained at 60 °C were significantly low compared to those by the other temperatures. The reason for low concentration at 60 °C is considered to be due to the incomplete dissolution of ABS samples in THF. For 90 °C and 120 °C, observed concentrations were comparable to those obtained by UE, further, corresponded approximately to those of prepared concentrations, *viz.* DP: 500 mg/kg; TBBPA and TPhP: 1000 mg/kg. The repeatabilities, represented as relative standard deviations (RSDs), at 90 °C and 120 °C were as follows: 1.8 %–8.7 % at 90 °C for 10 min; 1.3 %–3.6 % at 90 °C for 20 min; 0.8 %–3.4 % at 120 °C for 10 min; 1.2 %–2.2 % at 120 °C for 20 min. From the results of these repeatabilities, 90 °C for 10 min was a slightly poor repeatability because one ABS sample could not be dissolved in THF completely.

There was no significant increase for the concentrations with extended extraction time between 10 min and 20 min at 120 °C. Therefore, 90 °C for 20 min and 120 °C for 10 min seem to be suitable for the analysis, and in particular, 120 °C for 10 min is considered to be better because extraction time is short.

At 120 °C for 10 min, recovery yields were 100.4 % \pm 1.2 % for DP, 98.2 % \pm 2.2 % for TBBPA, and 101.0 % \pm 2.2 % for TPhP ($n = 3$; The values represent the mean \pm standard deviations; The values are described as percentage by the quantification results relative to the spiked amount of target FRs; Target concentration of recovery test was 500 mg/kg for DP and 1000 mg/kg for TBBPA and TPhP).

Influence of extraction solvent on MAE. Since the microwave-absorbing properties of the solvents affect the extraction efficiency, it is also important to select an appropriate solvent. Two solvents, *i.e.*, THF and Tol, were examined for the extraction of the target FRs. The effects of the extraction solvent are shown in Fig. 2 ($n = 3$; extracted at 120 °C for 10 min). Observed concentrations obtained with Tol were low compared to those with THF. The reason is considered to be due to the incomplete dissolution of ABS in Tol (at 120 °C for 10 min). Therefore, THF is suitable for recovering the target FRs from ABS in less time. A total ion chromatogram obtained by MAE with THF at 120 °C for 10 min is shown in Fig. 3.

Comparison of results obtained by MAE and UE. As UE has been used in previous studies^{3,4}, UE was employed as a reference method in this study to evaluate the performance of MAE. As shown in Figs. 1 and 2, the observed concentrations and repeatabilities of the analysis obtained with MAE (with THF at 90 °C for 20 min, at 120 °C for 10 min, and at 120 °C for 20 min) were comparable to those with UE. This indicates that MAE can be applied to the recovery of target FRs in ABS as effectively as UE. In addition, in our study, the time needed for MAE is considerably shorter than UE. Therefore, for example, MAE has an advantage over UE for the extraction of target FRs from a lot of field survey samples.

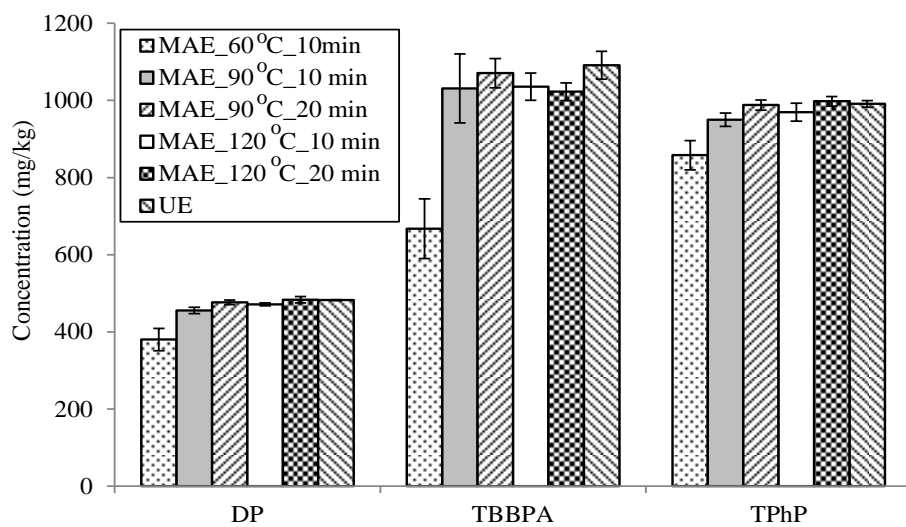


Fig. 1 Observed concentrations as a function of MAE temperature and time

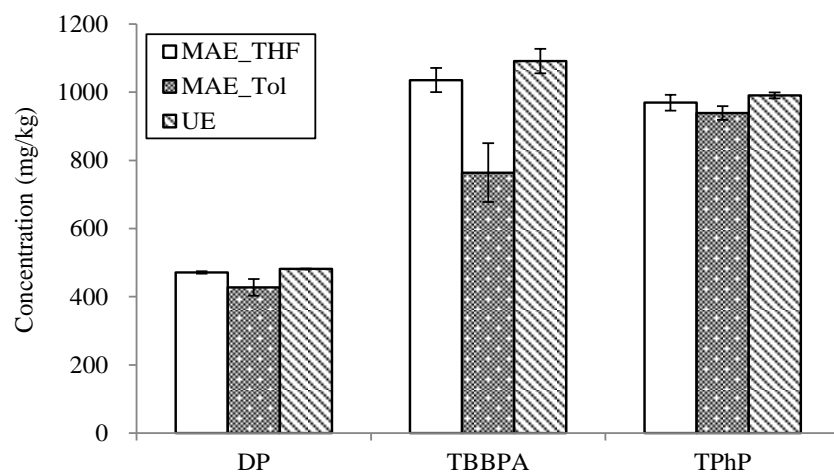


Fig. 2 Observed concentrations for 2 solvents using MAE
(The results for MAE_THF (extracted at 120 °C for 10 min) and UE (with THF for 60 min) are the same as those described in Fig. 1.)

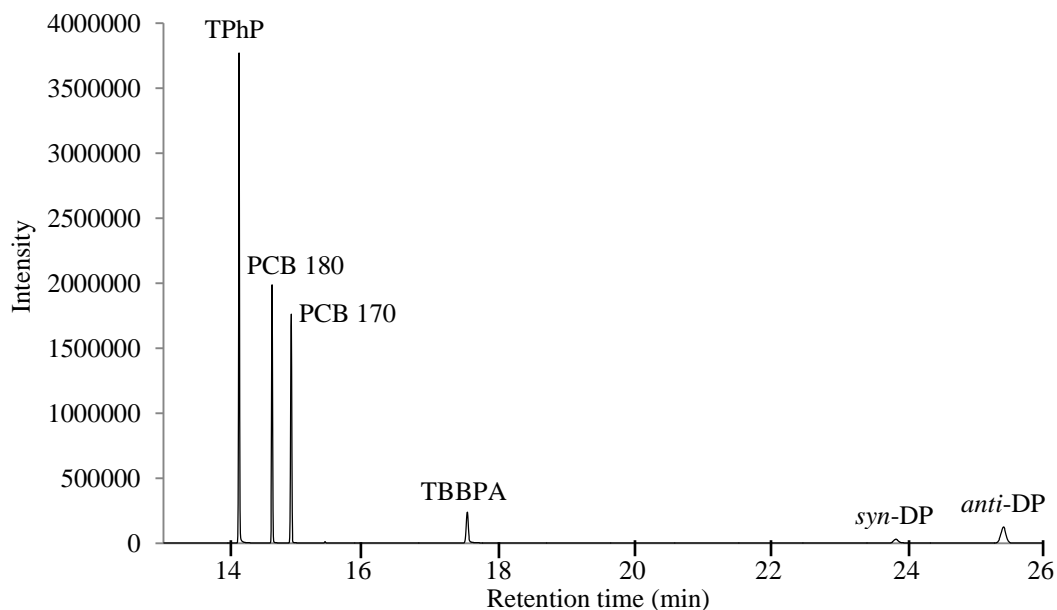


Fig. 3 Total ion chromatogram of target FRs obtained by MAE with THF at 120 °C for 10 min

Acknowledgements

This work was supported by the Environment Research and Technology Development Fund (3K 133009) of the Ministry of the Environment, Japan.

References

1. van der Veen I, de Boer J. (2012); *Chemosphere* 88: 1119-1153
2. Bergman Å, Rydén A, Law RJ, de Boer J, Covaci A, Alaee M, Birnbaum L, Petreas M, Rose M, Sakai S, den Eede NV, van der Veen I. (2012); *Environ Int.* 49: 57-82
3. Kajiwara N, Noma Y, Takigami H. (2008); *Environ Sci Technol.* 42: 4404-9
4. Chen Y, Li J, Chen L, Chen S, Diao W. (2012); *Procedia Environ Sci.* 16: 552-9
5. Bélanger JMR, Paré JRJ. (2006); *Anal Bioanal Chem.* 386: 1049-58
6. Camel V. (2001); *Analyst* 126: 1182-93