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Accurate determination and certification of bromine in plastic by isotope dilution inductively coupled plasma mass spectrometry

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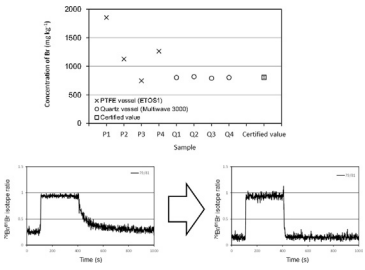
HIGHLIGHTS

- Accurate analytical method of Br in plastic was studied by isotope dilution ICPMS.
- A microwave acid digestion using quartz vessel was suitable for Br analysis.
- Sample dilution by NH_3 solution could remove memory effect for ICPMS measurement.
- The analytical result of the ID-ICPMS showed consistency with that of INAA.
- The ID-ICPMS developed could apply to certification of Br in candidate plastic CRM.

GRAPHICAL ABSTRACT



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ABSTRACT

The accurate analytical method of bromine (Br) in plastic was developed by an isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS). The figures of merit of microwave acid digestion procedures using polytetrafluoroethylene (PTFE) or quartz vessels were studied and the latter one was suitable for Br analysis since its material was free from Br contamination. The sample dilution procedures using Milli-Q water or ammonium (NH_3) solution were also studied to remove memory effect for ICPMS measurement. Although severe memory effect was observed on Milli-Q water dilution, NH_3 solution could remove it successfully. The accuracy of the ID-ICPMS was validated by a certified reference material (CRM) as well as the comparison with the analytical result obtained by an instrumental neutron activation analysis (INAA) as different analytical method. From these results, the ID-ICPMS developed in the present study could be evaluated as accurate analytical method of Br in plastic materials and it could apply to certification of Br in candidate plastic CRM with respect to such regulations related to RoHS (restriction of the use of hazardous substances in electrical and electronics equipment) directive.

1. Introduction

EU (European Union) legislated the RoHS (restriction of the use of hazardous substances in electrical and electronics equipment) directive since July, 2006 [1,2]. The directive restricted the concentration of such hazardous substances as Cd, Cr(VI), Hg,

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Pb, PBB (poly-brominated biphenyl) and PBDE (poly-brominated diphenyl ether) in electrical and electronics equipment produced in EU and transported from other areas. In recent years, several large companies such as Apple Inc. and Samsung also set their own internal regulations for their quality control and risk management on the concentrations of total bromine (Br) and total chlorine (Cl) in their products [3,4]. The threshold value of their internal regulations is 900 mg kg^{-1} for Br or Cl if both elements are not mixed in the materials. On the other hand, 1500 mg kg^{-1} is set as their threshold values if Br and Cl are coexisted. Because many plastics are well known to be used widely in electrical and electronics equipment, the analytical methods for Br and Cl in plastics are of importance and interest in the industries as well as relevant societies. In case of Br and Cl analysis in solid samples, an ion chromatography (IC) with combustion method [5–10], a thermal ionization mass spectrometry (TIMS) with combustion method [11–14], an inductively coupled plasma optical emission spectrometry (ICPOES) or inductively couple plasma mass spectrometry (ICPMS) with combustion method [15–17], a X-ray fluorescence (XRF) spectrometry [18–22] have been applied so far. The recovery in combustion process is the subject to achieve the accurate determination for IC, TIMS, ICPOES and ICPMS. The different mass absorption between sample and standard is the subject for XRF spectrometry. The certified reference material (CRM) would be effective for the validation of these analytical methods mentioned above. In order to develop a CRM, several analytical methods are recommended to be applied to determine the certified value [23,24]. An ICPMS has proven to be a powerful tool for quantitative multielement analysis as well as isotope ratio determination due to its high sensitivity, multielement capability, and wide linear dynamic range [25,26]. An isotope dilution ID-ICPMS is known to be a primary method of measurements, which is one of the reliable analytical methods; therefore, it is recommended to be applied for the CRM development [14,27–34]. Even though the ID-ICPMS is reliable, its validation is essential before certification.

The purpose of the present study is the development of ID-ICPMS for accurate determination of Br in plastics. The microwave acid digestion procedures with different vessels as well as different dilution procedures of digested sample solution using Milli-Q water or ammonium (NH_3) solution were examined. The accuracy of ID-ICPMS was validated by another CRM as well as the comparison with analytical result obtained by an instrumental neutron activation analysis (INAA), which was expected as a complementary analytical method since it allowed direct element analysis in solid materials neither any severe matrix effect nor any loss of elements concerned during sample pretreatment procedures [35–42]. The ID-ICPMS developed in the present study could be evaluated as accurate analytical method and it was applied to the certification of Br in candidate plastic CRM with respect to such regulations related to RoHS directive.

2. Experimental

2.1. Instruments

The microwave acid digestion systems used were an ETHOS 1 (Milestone S.r.l., Sorisole (BG), Italy) and a Multiwave 3000 (Anton Paar® GmbH, Graz, Austria). The polytetrafluoroethylene (PTFE) vessel of HPR1000/10 rotor was used for ETHOS 1. On the other hand, the quartz vessel (XQ80) of 8NXQ80 rotor was used for Multiwave 3000. The microwave heating programs were shown in Tables 1a and 1b, for ETHOS 1 and Multiwave 3000, respectively. Cleaning of the PTFE or quartz vessels for the microwave acid digestion system was performed using 8 mL of 68% HNO_3 (Ultrapur, Kanto Chemical Co. Inc., Japan) by each microwave heating program. The vessels were rinsed more than three times by Milli-Q water (Milli-Q Element, Millipore, Tokyo, Japan) after microwave heating, and the dry ones were used for microwave acid digestion. An instrumental neutron activation analysis (INAA) was also carried out for the determination of Br in plastics as different analytical method from the ID-ICPMS. Neutron radiation to plastics as well as calibration standards of Br was conducted by the Kyoto University Research Reactor (KUR) at Kyoto University Research Reactor Institute (KURRI, Kyoto, Japan). The radiation power, the thermal neutron flux and the radiation time were 1 MW, 8×10^{10}–5×10^{12} cm^{-2} s^{-1} and 10–30 min, respectively. After the radiation, gamma ray from the plastics and calibration standards was measured by a Ge semiconductor detector. The details are described in [42]. The ICPMS instruments used was an Agilent 7500cs (Agilent Tech. Inc., Tokyo, Japan) and its operating condition was summarized in Table 2 for both the ID-ICPMS and the laser ablation (LA)-ICPMS. The LA system was UP-213 (Electro Scientific Industries Inc., Portland, OR, USA) and the homogeneity of Br in each one pellet was evaluated from 30 pellets, which were taken from 30 bottles randomly selected, by LA-ICPMS with single spot ablation mode of LA as listed in Table 3, since the LA allowed the local analysis within one pellet. The ^{13}C signal measured was used as an internal standard to compensate signal fluctuations of ^{79}Br and ^{81}Br obtained by LA-ICPMS.

Table 1a
Microwave heating program of ETHOS 1.

	Temperature	Time
Step 1	20 °C → 80 °C	3 min
Step 2	80 °C → 50 °C	2 min
Step 3	50 °C → 150 °C	5 min
Step 4	150 °C → 200 °C	5 min
Step 5	200 °C → 220 °C	5 min
Step 6	220 °C	35 min
Step 7	Ventillation	20 min

2.2. Samples

The sample was polypropylene (PP) resin pellet, which was candidate CRM for Br analysis produced by NMIJ. In order to prepare candidate PP resin pellet CRM that contained ca. >300 mg kg^{-1} of Br, certain amounts of decabromodiphenyl ether (DBDE, 98%, Sigma–Aldrich Co. LLC, USA) and base PP resin pellet was mixed by dry blend in a plastic bag. The mixed material was extruded by an extruder at 200 °C; then, the extruded plastic was pelletized by a pelletizer and homogenized. The preparation procedure from extrusion to homogenization was carried out for total of three times to achieve sufficient homogeneity of Br in the candidate PP resin pellet CRM. The preparation procedure mentioned above was similar to that of our previous work [32,33]. The final PP resin pellet obtained was ca. >10 mg for each one pellet (ca. > 2 mm, ca. > 3 mm and ca. > 1 mm in width, length and thickness, respectively). The measured density of the PP resin pellet was 0.8990 ± 0.0103 g cm^{-3} ($k = 2$). Before weighing the pellet, it was dried at 80 °C for 1 h in an electric oven and cooled in a desiccator with silica gel for 1 h to remove any moisture [32,33]. The CRM of BCR 680 (Trace elements in polyethylene (high level), Institute for Reference Materials and Measurements, Geel, Belgium) [11,12,28] was used to evaluate different microwave

Table 1b
Microwave heating program of Multiwave 3000.

	Power	Ramp	Hold
Step 1	1000 W	30 min	60 min
Step 2		Cooling	60 min