EVALUATION OF BROMINATED FLAME RETARDANTS BY ION ATTACHMENT MASS SPECTROMETRY

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Introduction

In view of a strong demand for products with minimal impact on humans and the environment for the purpose of protecting and improving environmental quality and of protecting human health, controls on certain substances used in products and their materials are being imposed[1, 2]. In the European Union, six substances such as Lead (Pb), Cadmium (Cd), Mercury (Hg), Hexavalent Chromium (Cr^{6+}), and two types of brominated flame retardants (like Polybrominated Biphenyls: PBB, Polybrominated Diphenyl Ethers: PBDE) are prohibited for use in electrical and electronic equipment from the 1st of July 2006 according to European legislation for the directive on the limitation of hazardous substances in electrical and electronic equipment (RoHS directives)[3]. Even when such hazardous substances are removed from materials in the near future, monitoring of these controlled substances is necessary to ensure compliance with the restrictions on their use.

Gas Chromatograph Mass Spectrometry (GC-MS) is well known as an analytical method for brominated flame retardants[4], however, it requires much time and complicated sample treatment. Whereas, Ion Attachment Mass Spectrometry (IAMS) which enables to measure the elements in solid organic compounds directly has been developed[5]. In the IAMS measurement, the sample is ionized with lithium ion and introduced to mass spectrometer as lithium – attached compounds. Because this ionization method is very soft, no fragment peaks appear in the mass spectrum. This feature is thought to be applied for the quality control of the flame retardants to determine the levels restricted substances in electro technical products. In this report, we present a new reliable analytical method for the brominated flame retardants by IAMS, and discuss its application to electro technical products.

Materials and Method

The certified reference material used was NMIJ CRM 8106-a (National Institute of Advanced Industrial Science and Technology, Japan). It is made of polystyrene and the certified value of decabromodiphenylether (DeBDE)

is 317 ppm. The IAMS instrument used was IA-Lab L-250G-IA (Canon Anelva Technix Co., Japan). The sample was heated to 300℃ and vaporized by the infrared lamp. Both ion attachment (IA) and electron impact (EI) ionization method were used. After ionization, constituents were measured in mass spectrometer.

Results and Discussion

The certified reference material was analyzed by IAMS and measured the concentration of DeBDE. The result is as shown in Figure 1. The concentration of DeBDE calculated from the peak area was 270 ppm. The measurement error of IAMS for DeBDE was less than 20%. It shows that IAMS is an applicable method for the analysis of brominated flame retardants.

In the case of TBBPA-BP (tetrabromobisphenolA-bis(dibromopropylether)), EI method was also applied. Because the ionization of IAMS is very soft, only a molecular ion peak is detected in IAMS measurement. However, this makes it difficult to assure the identification of the constituents whose masses are close to each other. For example, the masses of TBBPA-BP (Mw=943.61) and DeBB (decabromobiphenyl, Mw=943.17) are almost the same. DeBB is regulated by RoHS directive. In order to distinguish these two constituents, EI method was adapted. When they were measured by EI method, two different types of fragment peaks were obtained as shown in Figure 2. The fragment patterns of TBBPA-BP and DeBB were analyzed as shown in Figure 3. By using EI method, the characteristic fragment peaks for each constituent were obtained, and then the two constituents could be distinguished. When it was difficult to distinguish the constituents because of their similar masses in IA method, they were identified by using together with EI method.

The plastic samples added other brominated flame retardants such as TBBPA (tetrabromobisphenolA), BPBPE (bis(pentabromophenyl)ethane) and EBTBPI (ethylenebis(tetrabromophthalimide)) were also prepared and measured by IAMS. The results of TBBPA are shown in Figure 4. The molecular ion peak of TBBPA (m/z: 551) was detected by IA method and the fragment peaks (m/z: 293, 529) were detected by EI method. The same results were obtained for BPBPE and EBTBPI. It was found that the brominated flame retardants in plastics were measured easily and quickly by IAMS.

IAMS method can be successively applied for quality control to check the contents of brominated flame retardants in plastics.

References:

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3. Directive 2002/95/EC of European Parliament and of the Council on the Restriction of the Use of Certain Hazardous Substances in Electrical and Electronic Equipment *the Official Journal of European Union* 2003; 19: L37.
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Figure 1: Chromatography and mass spectrum for DeBDE in IAMS

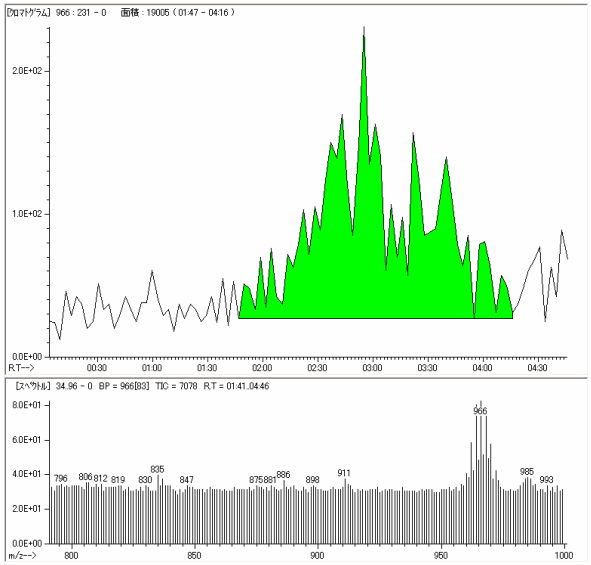


Figure 2: Mass spectra using EI method

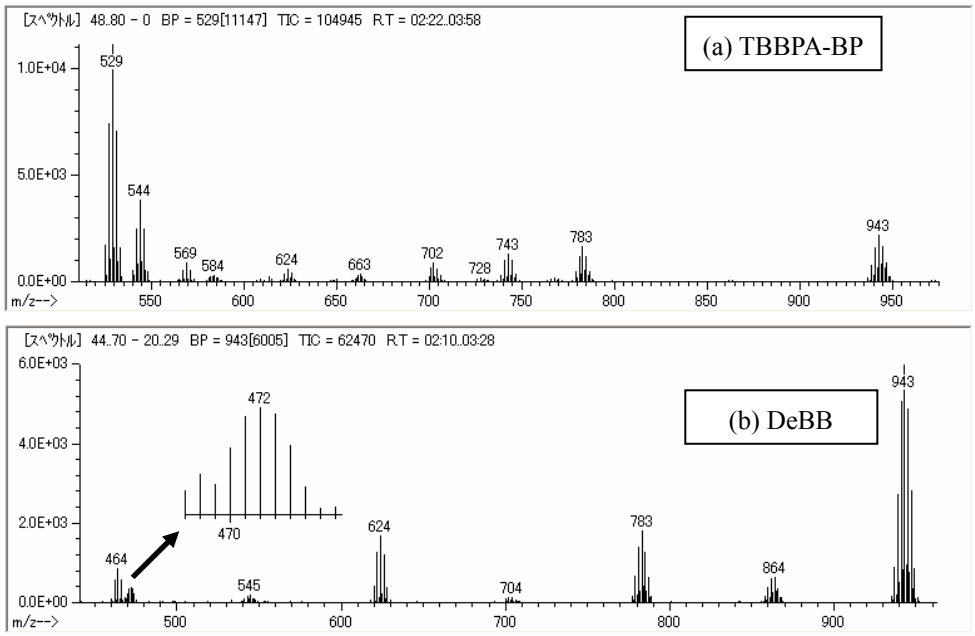
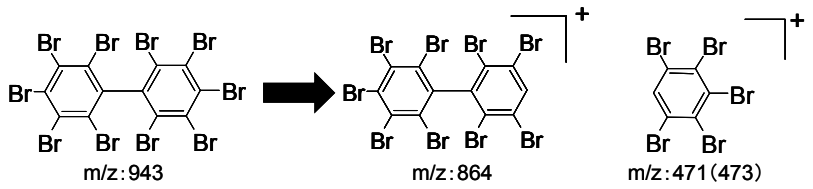
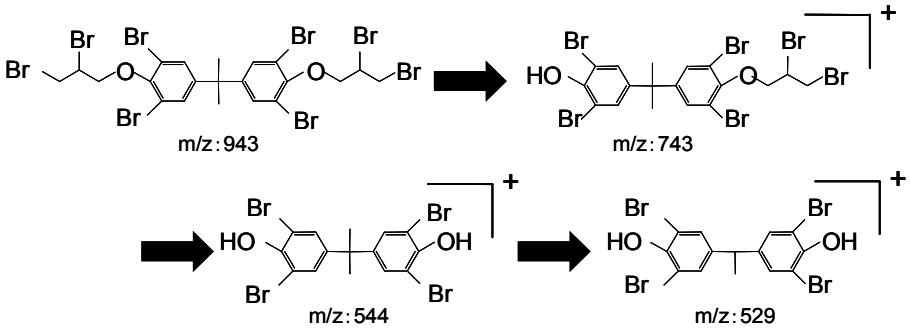


Figure 3: The fragment patterns of TBBPA-BP and DeBB



(a) DeBB



(b) TBBPA-BP

Figure 4: Mass spectra of TBBPA in IAMS