SHIMADZU APPLICATION NEWS

LAAN-A-AA-E012

● SPECTROPHOTOMETRIC ANALYSIS

No.A375

Screening Analysis of Brominated Flame Retardants with ATR Accessory (Part 3) - RoHS Directive-

In previous Application News publications (No. A358, No. A363), the regulated substance PBDE (polybrominated diphenyl ether) was introduced with respect to the effects of PBDE and additives in plastics, however, there is another kind of brominated flame retardant that will actually be regulated. Here we introduce the regulated substance PBB (polybromobiphenyl).

■ Sample

Fig.1 shows the structure of polybromobiphenyl, specified as one of the substances to be regulated by the RoHS directive. This substance, like PBDE (especially, penta-BDE), is a flame retardant that accumulates in living bodies. When this substance accumulates in the living body, it can affect the skin, liver function, thyroid gland and immune system, so it is an extremely toxic substance to the human body.

As clearly shown in Fig.1, many isomers exist in PBB. The compound formally used as a retardant consisted of 6 bromines, hexabromobiphenyl (HBB), as the main ingredient, but as a mixture of 5, 6 and 7 bromines, was commercially available as “Firemaster”. Compounds with other numbers of bromine those include octobromobiphenyl (OBB), with 8 bromines, and decabromobiphenyl (DBB), with 10 bromines were distributed worldwide. PBBs were chiefly mixed with ABS resin, and used in small tool materials, automobile paints, coating lacquer, and polyurethane foam, etc. Commercial production of “Firemaster” started in 1970 in the United States, and was permanently discontinued in 1974 due to the Michigan contamination incident. Since the final production of DBB in France in May, 2001, PBBs have not been produced in any country in the world (There has never been domestic demand for PBBs in Japan.). However, the possibility that PBB was used as a fire retardant in plastics before 2001 cannot be denied. Here we report on an evaluation of PBB in plastic that we conducted.

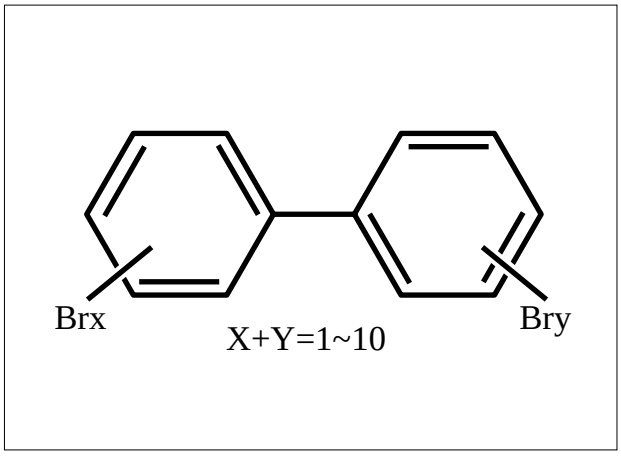

Fig.1 Structure of Polybromobiphenyl

■ Spectrum of Decabromobiphenyl (DBB)

The fire retardant we used for measurement was the 10-substitution compound decabromobiphenyl (DBB). The analytical conditions are shown in Table 1.

Table 1 Analytical Conditions

Resolution	: 4cm^{-1}
Accumulation	: 20
Detector	: DLATGS

The DBB spectrum was measured using the conditions shown in Table 1. The obtained spectrum is shown in Fig.2.
A strong intensity peak of DBB can be seen in the vicinity of 1350 – 1200cm^{-1} in Fig.2. Moreover, compared to PBDE, some small peaks appear at the lower wave numbers (in the case of PBDE, there is a strong intensity peak near 1350cm^{-1}).
Next, we investigated how the spectrum was changed when the DBB was included in plastic. Fig.3 shows overlaid spectra of standard polystyrene and polystyrene containing 5wt% DBB. And, a close-up of the spectra in the vicinity of 1700 – 1200cm^{-1} of Fig.3 is shown in Fig.4. The blue profile is spectrum of the standard polystyrene, and the red profile is that of the polystyrene containing the 5wt% DBB.
In Fig.4, the peak derive from DBB in the polystyrene is clearly seen in the vicinity of 1300cm^{-1}. We believe that the existence of DBB in plastic can be evaluated using this peak.

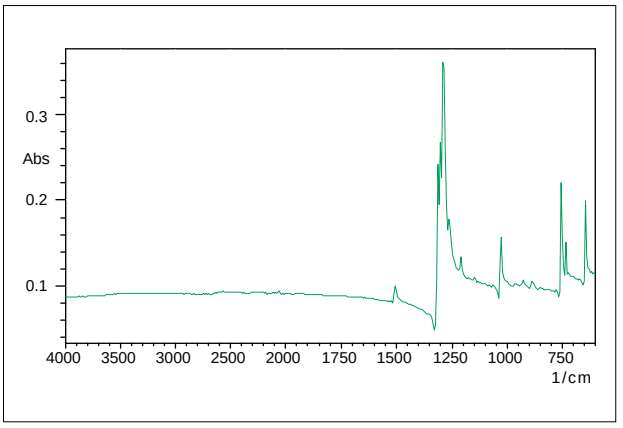

Fig.2 Spectrum of DBB

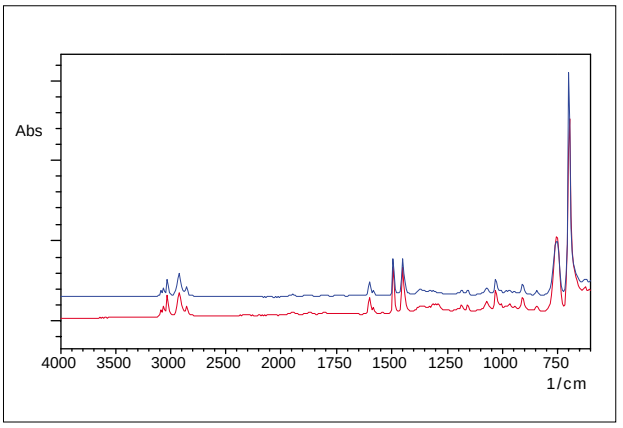

Fig.3 Spectra of Standard and 5wt% DBB-containing Polystyrene

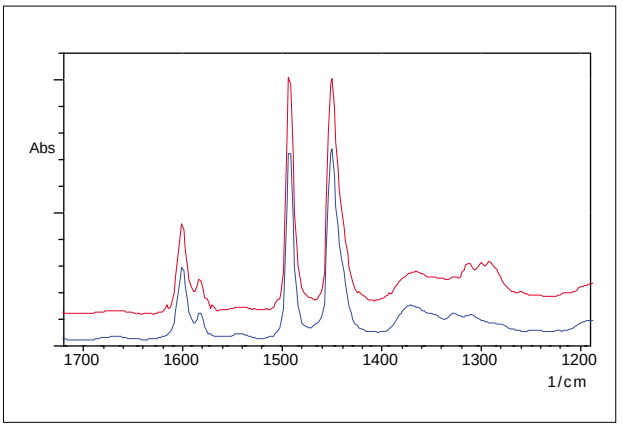

Fig.4 Enlarged Spectra of Fig.3

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