Screening Analysis of Brominated Flame Retardants with ATR Accessory (1) (RoHS Directive)

Plastics used for electrical and electronic components contain several percent brominated flame retardants. Two types of brominated flame retardants will be restricted under the RoHS directive implemented by the EU in July 2006. We introduce here an example of screening analysis for brominated flame retardant using the single reflection ATR accessory provided with the FTIR spectrophotometer.

■ RoHS Directive
The RoHS (Restriction of Hazardous Substances) directive, which will be enforced in the EU in July 2006, will regulate the use of specific hazardous substances in electrical and electronic products. The following six substances will be controlled: Pb, Hg, Cd, Cr⁶⁺, polybromobiphenyl (PBB), and polybromodiphenylether (PBDE). In compliance with this directive, manufacturers are required to prevent or stop the use of these substances in their products to be marketed in the EU countries. (At present specific concentrations are not yet decided. However, it is expected that the concentration limit for brominated flame retardants will be under 1000ppm.)

■ Sample
Two types of brominated flame retardants are subject to the RoHS Directive, of which decabromodiphenylether (DBDPE) was analyzed here. Fig. 2 shows the structure of DBDPE.

The test sample used was polystyrene containing 5wt% of DBDPE. With general plastics, ppm-levels of flame retardant does not provide a flame-retardant effect. To obtain a sufficient level of flame-retardant effect, 5-10wt% of flame retardant is required. Therefore, in this analysis, 5wt% of flame retardant was added to the test sample.

The other flame retardant to be regulated, PBB, is not used in Japan. So it is omitted here.

■ Measurement Method
Measurements were carried out using the single reflection ATR accessory DuraSampIR-Ⅱ System I (see Fig. 1). The plastic sample is pressed directly against the prism for analysis. The analytical conditions are shown in Table 1.

<table>
<thead>
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<th>Table 1 Analytical conditions</th>
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<td>Resolution</td>
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<td>Accumulation</td>
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<td>Detector</td>
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4.0cm⁻¹
20
DLATGS

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- Metal plate (316 S/S or Hastelloy)
- Plastic sample
- Diamond ATR prism
- ZnSe (KRS-5) support element
- Infrared light

Fig. 2 Structure of Decabromodiphenylether (DBDPE)
Spectra of Plastics in Electronic Products

Fig. 3 shows the spectra of polystyrene (PS), DBDPE, and polystyrene containing 5wt% of DBDPE.

In the spectrum of the PS containing 5wt% of DBDPE, the peak of DBDPE near 1350cm⁻¹ overlaps with the peak of PS.

Judgement in the Macro Program

Fig. 4 shows the results of judgement by a macro program of whether brominated flame retardant is contained or not, in plastic from the measured spectrum. The test sample was a television component. The macro program judgement that the test sample was polystyrene containing DBDPE. This macro program automates the series of operations from measurement to judgement and report output.

Analysis of Brominated Flame Retardants in case of Low Concentration

As introduced above, brominated flame retardants in the order of % can be analyzed using the FTIR. However, ppm-levels of analysis requires GCMS. Fig. 5 shows the mass spectra of polystyrene (PS) containing 0.1wt% of DBDPE.

In Fig. 5, 1000ppm DBDPE (peak E) is detected with good sensitivity. Because this analysis involved thermal extraction, part of the flame retardant was decomposed and detected in nine substituted forms (peaks B, C, and D).

As shown above, brominated flame retardants contained in electrical and electronic products can be analyzed using FTIR or GCMS. FTIR is more suitable for screening, while GCMS with solvent extraction is more suitable for precision analysis. For further details of analysis using GCMS, refer to “Analysis of Brominated Flame Retardants by Evolved Gas Analysis” (Application News No. M222).