

Quantitative analysis of red phosphorus flame retardant in polybutylene terephthalate by evolved gas analysis (EGA)-MS

[Background] Red phosphorus has been used as an alternative material to brominated flame retardants, and quantitative analysis of red phosphorus flame retardants in polymeric materials has been carried out by pyrolysis (Py)-GC/MS¹⁾ and EGA-MS.²⁾ Generally, separation of red phosphorus from polymer is cumbersome and difficult due to the insolubility of red phosphorus. Red phosphorus is converted to phosphorus tetramers (P₄) when rapidly heated under inert atmosphere, *i.e.* pyrolyzed, as shown in Fig. 1. Since P₄ shows a strong molecular ion peak (m/z 124) in its mass spectrum (Fig. 1), the molecular ion peak in pyrograms and thermograms can be used for qualitative and quantitative analysis of red phosphorus. This note describes the quantitative analysis of red phosphorus in polybutylene terephthalate (PBT) by EGA-MS.

[Experimental] A PBT sample containing ca. 6 wt% of red phosphorus was milled into a powder (particle diameter 50-100 μm) and 0.2 mg of the sample powder was placed in an inert SS sample cup. The EGA-MS system consisted of a Multi-Shot pyrolyzer (EGA/PY-3030D, Frontier Labs) interfaced directly to the GC/MS split injection port. The temperature was increased from 100 to 600°C at 20 °C/min. Determination of red phosphorus was done based on the m/z 124 peak area on EGA thermograms. A linear calibration curve (correlation coefficient, $r = 0.999$) was obtained by using the red phosphorus standard sample.

[Results] The EGA thermogram of a PBT sample containing red phosphorus is shown in Fig. 2. Fragment ions from PBT and the molecular ion of P₄ (m/z 124) are observed in the averaged mass spectrum of the EGA thermal zone of 285-550°C. The extracted ion thermogram (m/z 124) indicates that P₄ is evolved between 360 and 510°C. The concentration of red phosphorus in the PBT sample was determined to be 5.9 wt% (RSD=1.9%, $n=5$). This value agreed well with the original formulation and was close to the concentration (6.1 wt%) determined by Py-GC/MS.

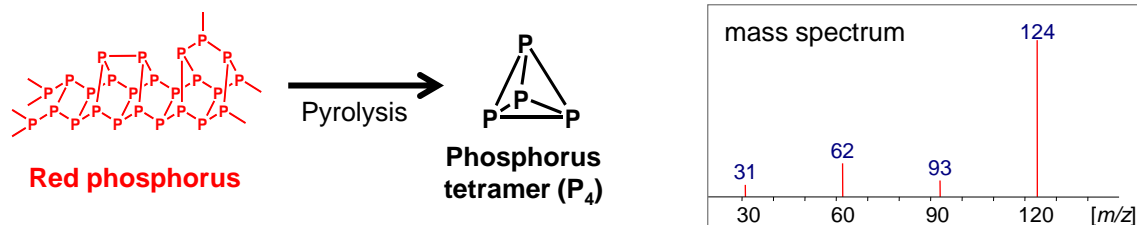


Fig.1 Pyrolysis of red phosphorus and mass spectrum of phosphorus tetramer

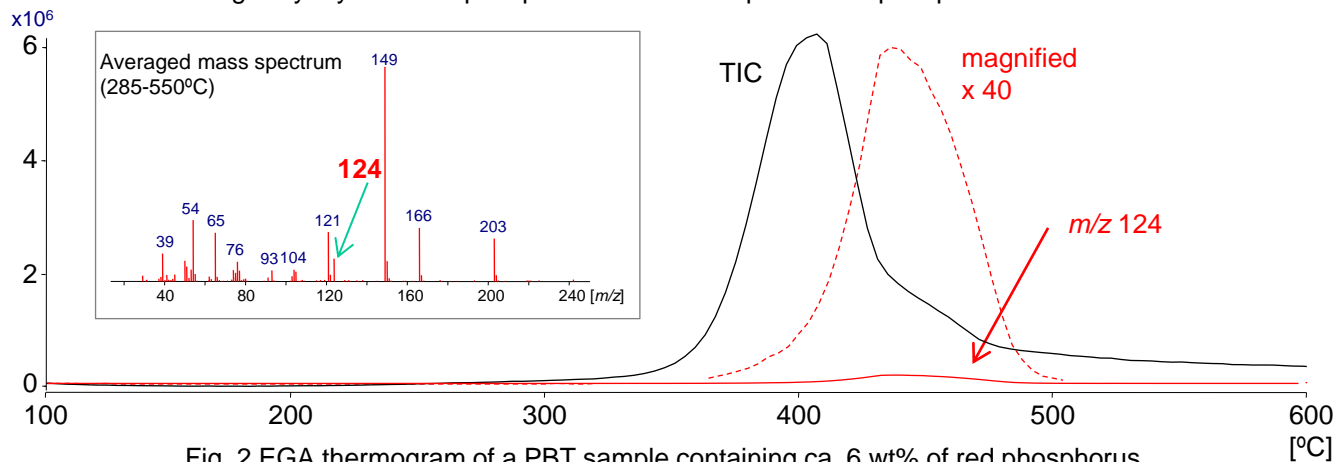


Fig. 2 EGA thermogram of a PBT sample containing ca. 6 wt% of red phosphorus.

Furnace temp.: 100-600°C (20 °C/min), GC oven temp.: 300°C

EGA tube: deactivated metal tube. L=2.5 m, i.d.=0.15 mm, Column flow rate: 1 mL/min He, Split ratio: 1/50, Sample wt: 0.2 mg

1) M. Iida, *et al.*, *Anal. Sci.* 2008, 24, 539-542. 2) T. Ishimura, *et al.*, 20th Polym. Anal. & Characterization, 2015.

Keywords : EGA-MS, flame retardant, red phosphorus, polybutylene terephthalate, quantitative analysis

Applications : Product inspection, quality control

Related technical notes :

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R&D and manufactured by :
Frontier Laboratories Ltd.

4-16-20 Saikon, Koriyama,
Fukushima 963-8862 JAPAN
Phone: (81)24-935-5100 Fax: (81)24-935-5102
<http://www.frontier-lab.com/>