

THE RAPID ANALYSIS OF PBDEs (POLY BROMINATED DIPHENYL ETHERS) UTILIZATING THE ION ATTACHMENT MASS SPECTROMETRY

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Abstract

Poly Brominated Biphenyls (PBBs) and Poly Brominated Diphenyl Ethers (PBDEs) in resin were measured utilizing the "Ion Attachment Mass Spectrometry" (IAMS), this new measuring method takes only 5min for identifying PBDE and 30min for the quantification. It is approximately 100 times faster than the present method of GC-MS with solvent extraction for identification, Furthermore, IAMS appears to be advantageous for determination of congeners. The systems show little decomposition of samples.

Introduction

PBBs and PBDEs, which are contained in resins for industrial materials as a flame retardant, are restricted from use by the European RoHS Directives as of July 2006. Every electrical manufacture has to ascertain their products to be acceptable by RoHS directives. A simple and easy method for high throughput screening is strongly required. Fluorescent X ray as rapid analysis cannot distinguish PBDEs from many other kinds of brominated flame retardants. GC/MS with solvent extraction takes several hours for each sample, due to the complicated preparation (extraction) and GC separation. In our study, we will report the capability of the IAMS for rapid analysis of the PBDEs.

With the IAMS, our instrument is based on the Fujii et. al.¹, principle, an alkaline metal ion attaches to a molecule by the Coulomb force, with the excess energy being lower than the binding energy among the atoms, only the molecular peak coming from the original component, appears without any fragment peaks. This means, we can locate the component peak even in labile compounds.

Methods

<Reagents>

Sample solution in tetrahydrofran was poured into the cup (4mm x 3mm) made of SUS. After solvent disappeared, the cup was placed into the DIP (direct inlet probe). The DIP is transferred into the ionization chamber, where the sample is heated and the gaseous components are extracted from the sample and a measurement process is performed. (Fig. 1)

<resin samples with PBDEs>

Small Samples are removed by scraping or snipping, about 1mg from the sample material and placed into the DIP. It has done like the above-mentioned. For quantification, the resin samples were pulverized with a freeze-grinder.

We investigated some types of Brominated Flame Retardants(HBCD, TBBPA, BPBPE, etc.), 10 standard resins which include DeBDE with known contents, many other actual resin samples (approximately 2000 actual practical resin samples) have been measured.

Results and Discussion

<Identification Analysis>

OcbDE (commercially available as a mixture of PBDEs) was measured with the IAMS. The spectrum shows each apparent congeners. (Fig. 2) IAMS is able to detect the congeners of PBDEs.

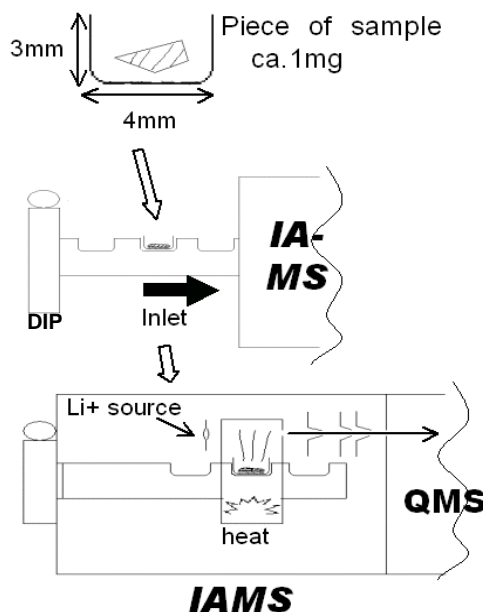


Fig.1 How to measure

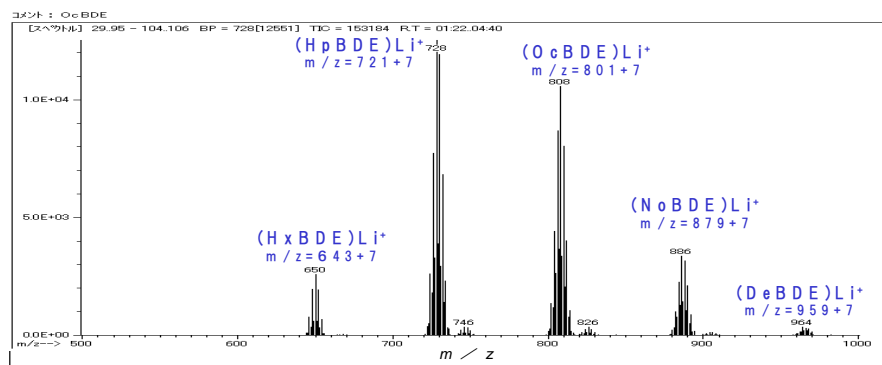


Fig.2 IAMS spectrum of OcBDE (commercially available as a mixture of PBDEs)

<Determination Analysis>

Calibration curves of DeBDE standard solution and ABS resin containing DeBDE (01%, 0.96% and 9.8%) has indicated a good correlation coefficient (0.996) and recovery rate of (>90%). (Fig. 3)

According to the results of several resin samples with known quantities (Table), the practical detection limit are less than 100 ppm, lower than regulated value of 1000 ppm in RoHS. Comparing the amount of detected DeBDE, there was a good correlation between the conventional method, GC-MS with solvent extraction and IAMS. Practically all samples, RSD was <20%. This value is acceptable for the repeatability requirements for RoHS Directives. IAMS has shown the potential ability to perform determination regardless of the type of resin.

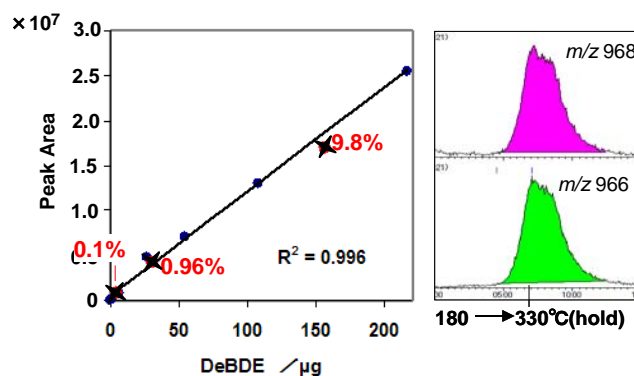


Fig.3 Calibration curve of DeBDE

Table Influence of resin

	Base resin	DeBDE content		
		GC/MS*	IAMS*	RSD%(n)
1	PS	2100	2800	6.5(3)
2	PE	900	1100	12.1(3)
3	ABS	1000	960	9.5(5)
4	m-PPE	1000	960	12.2(5)
5	PA6	850	980	10.4(3)
6	PBT	990	1200	4.6(3)

PS; polystyrene, PE; polyethylene, m-PPE; degeneration polyphenylene ether, PA6: polyamide, PBT; polybutyrene terephthalate

*)GC/MS is with solvent extraction, IAMS hold the thermal extraction part

Conclusion

We established the new rapid measurement system of PBDEs with IAMS can comply to the RoHS Directives.

References

1. Fujii, T. *Mass Spectrometry Review*, 19,(2000) 111.
2. Y.shiokawa et al, *Bunseki Kagaku*, 53,(2004) 475