Analysis of halogenated phosphorus flame retardants in insulating foam using pyrolysis and high resolution gas chromatography

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Introduction

Polyurethanes are a diverse group of polymers used in a wide array of products including furniture, automotive interiors, bedding, packaging, carpet underlayment and general household insulation. Flame retardants (FRs) are added to these polyurethanes in order to meet flammability standards. Unfortunately, many of these FRs, such as polybrominated diphenyl ethers (PBDEs) have adverse health effects which have led to their restriction or elimination in many countries. Phosphorus flame retardants (PFRs) have emerged over a period of time as replacements for PBDEs. Regrettably, basic information such as chemical identity, environmental and human health impact have not been well-documented.[1,2] In fact, it has been suggested that halogenated PFRs are not suitable alternatives for BFRs since they are bioaccumulative and may be toxic (e.g., carcinogenic).[3] The goal if this study was to use pyrolysis gas chromatography/high resolution mass spectrometry (Py/GC-HRT) to characterize polyurethane foam.

Materials and methods

Pyrolysis is the breakdown of materials using thermal energy. This resulted in smaller, volatile and therefore GC amenable analytes. Pyrolysis minimized sample preparation and requires=d only trimming and weighing of solid samples into quartz tubes. GC-HRT instrumentation facilitated fast and comprehensive data collection for full characterization of samples. Pyrolysis was conducted using a CDS Analytical Pyroprobe 2000 mounted on an Agilent split/spltless injector. The coil pyrolysis probe was operated at a temperature of 600 °C for a period of 10s. The GC was equipped with an R*xi*-5ms column (30m x 0.25mm x 0.25µm). The inlet was split 100:1 and set to 320 °C. The carrier gas flow was 1.0 mL/min and the oven temperature program was 40 °C (4 min) to 100 °C @ 8 °C/min, to 320 °C @ 20 °C/min. The GC-HRT acquired electron ionization data at 10 spectra per second with a mass range of 35-510. Chemical ionization (CI) data was also acquired, but with a mass range of 60-600 m/z. Data were processed using comprehensive, untargeted Peak Find. Monomers, additives and other compounds were characterized using a combination of spectral similarity searches of deconvoluted spectra against large, well-established databases and formula determinations for high resolution accurate mass fragment, molecular and adduct ions. The implementation of novel spectral analysis tools aided in the characterization of PFRs in the polyurethane sample.

Results and discussion

Processing of Py/GC-HRT provided a wealth of information on expected polyurethane components, as well as some unexpected additives and contaminants. Monomers such as methylene(*p*-phenyl isocyanate) (MDI) and a variety of

halogenated PFRs were detected in the foam sample (Figure 1). The eXtracted Ion Chromatogram (XIC) expansion with high resolution accurate mass plot of m/z = 250.0739 and 277.0158 shows six of the PFRs found in the sample. In addition, the comprehensive nature of this analysis facilitated the discovery of a diverse group of compounds as illustrated in Table 1. These compounds included monomers, as well as aromatic, halogenated, and heterocyclic compounds. This representative set of compounds exhibited average spectral similarity and absolute mass accuracy values of 880/1000 and 0.54 PPM, respectively. It is clear from this study that Py/GC-HRT is an effective tool for the comprehensive characterization of polyurethane foam

Figure 1. A) TIC for a foam sample. B) XIC displaying a MDI and several PFRs in polyurethane foam

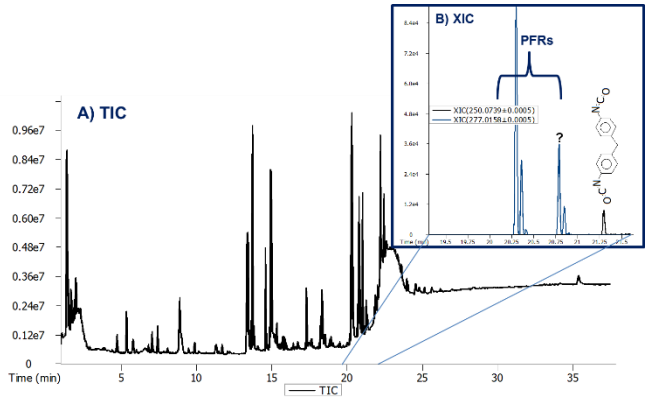

Table 1. Representative compounds in polyurethane

Name	*(ppm)*	*Similarity*
1-Propene, 3-bromo-	-0.05	897
p-Xylene	0.6	949
Benzene, isocyanato-	-0.21	948
Benzene, 1-ethyl-2-methyl-	0.5	867
1-Propenyl ester of carbonic acid	-1.32	853
4-Tolyl isocyanate	0.45	905
Benzene, 1,2-dibromo-	0.6	861
Benzene, 1,2,4-tribromo-	-0.35	945
Acridine	-0.06	924
Benzene, 1,2,4,5-tetrabromo-	-0.56	921
Acridine, 2-methyl-	0.11	879
1-anthracenamine	0.42	863
2-p-Tolylisoindole-1,3-dione	0.6	859

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