

BROMINATED DIOXINS AND OTHER BROMOAROMATICS IN PLASTIC PYROLYSATES

G. W. Sovocool*

U.S. Environmental Protection Agency, EMSL-LV,
P.O. Box 93478, Las Vegas, NV 89193-3478

J. R. Donnelly, A.H. Crange, R.D. Simmons, and W. D. Munslow
Lockheed Engineering & Sciences Co., Inc.,
1050 E. Flamingo, Las Vegas, NV 89119.

ABSTRACT:

Pyrolysates of polybutylene terephthalate resins, flame-retarded with decabromodiphenylether, were analyzed by GC/MS and found to contain brominated dioxins, dibenzofurans, naphthalenes, benzenes, toluenes, biphenyls, and methyl dibenzofurans. The bromomethyl dibenzofurans were identified by their mass spectra and comparison to the mass spectra of authentic standards.

INTRODUCTION:

The recent characterization of polybutylene terephthalate (PBT) thermoplastic resins, which had been flame-retarded with decabromodiphenylether, and their pyrolysates for brominated dioxins and dibenzofurans (PBDD, PBDF) introduced a question regarding the identity of a series of compounds (PBX) that interfere with the identification and quantification of the brominated dioxins.¹ These PBX compounds had mass spectra similar to the dioxins, but with molecular ions two Daltons lower. They were found in relative concentrations two to twelve times as high as the dioxins having the same numbers of bromine atoms. Because of the sample preparation scheme employed in these analyses, only planar aromatic compounds having no reactive functional groups would be expected. This report discusses the characterization of PBT resin pyrolysates for the broad range of bromoaromatics, and provides identification of the PBX class of analytical interferences.

EXPERIMENTAL:

Pyrolysate extracts were prepared as previously described¹, from 400°C and 600°C pyrolyses in the presence of oxygen.² They were analyzed by GC/MS, using selected ion monitoring and full-scan mass spectrometry. A Hewlett-Packard 5890 GC was fitted with on-column injection, a 60 m x 0.25 mm, 0.25 μ m film RT₊-5 column, helium carrier gas at 31 psi,

and a temperature program from 170°C (no initial hold) at 1°C/min to 320°C. The GC was coupled with a VG 70-250 SE mass spectrometer, 300°C transfer line, 270°C source, in electron ionization mode. Retention indices were calculated using the linear retention index scale for linear temperature programmed GC, against the normal hydrocarbons.

DISCUSSION:

Several series of brominated aromatic hydrocarbons were detected, including benzenes, toluenes, biphenyls, and naphthalenes. Tribromo- tetrabromo- and pentabromo-benzenes were found; in the bromobiphenyl series, 9 di-, 17 tri-, and 8 tetra-bromobiphenyls were chromatographically resolved. Similarly, 5 di- and 2 tri-bromonaphthalenes were present.

All chromatographically-resolvable polybromodibenzofurans (PBDF) were found for the mono-, di-, tri-, and tetra-bromo congeners. Several penta- and hexa congeners were not found, although expected to be resolvable under the GC conditions employed; missing isomers seemed to correlate well with the expected retention times for 1,9-substituted isomers. These isomers are less likely to be formed due to steric hindrance. The mass chromatograms and GC retention indices obtained for the PBDF are presented in Figure 1.

Synthetic standards of brominated xanthenes, xanthenes, and methyl dibenzofurans were prepared and analyzed. The 9,9-dibrominated xanthenes were either not prepared, or oxidized in situ to xanthenes during the synthesis. The xanthone carbonyl would prevent that class of compounds from passing through the sample preparation scheme. The brominated xanthene standards exhibited strong [M-H]⁺ and [M-Br]⁺ fragments; this intense [M-H]⁺ fragmentation was not seen in the isobaric pyrolysis components. On the other hand, some of the synthetic brominated methyl dibenzofurans (Me-PBDF) provided mass spectra very similar to those of the "PBX" unknowns in the pyrolysates. Under the synthetic reaction conditions, most of the Me-PBDF products were apparently ring-brominated and also side-chain brominated; they exhibited strong [M-Br]⁺ relative intensities, on the order of 50% (see Figure 2) as was seen in the corresponding pyrolysate components. A few standards were apparently only ring-brominated; they had low (ca. 10%) [M-Br]⁺ relative intensity and [M-2Br]⁺ base peak (see Figure 3). Therefore, it appears that the unknown PBX reported earlier as either brominated xanthenes or methyl dibenzofurans are the latter, with ring and methyl positions brominated.

In further support to the Me-PBDF (vs. xanthene) assignment, other (C₂ and C₃) alkyl-PBDF were found in the pyrolysates. Numerous congeners of ethyl (and/or dimethyl)-PBDF, and a few propyl (and/or trimethyl or ethylmethyl)-PBDF were detected. Mass spectra of standards indicated that brominated toluenes do not exhibit relatively intense [M-CH₃]⁺, but that ethylbenzenes do. The C₂- and C₃-alkyl-PBDF found in the pyrolysates exhibited relatively intense [M-CH₃]⁺ fragments, supporting the argument for ethyl, and propyl or ethylmethyl substitutions rather than dimethyl and trimethyl substitution patterns.

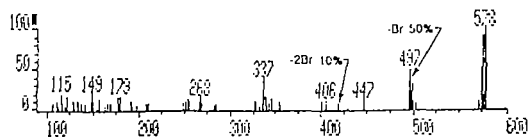


Figure 2. Methyl pentabromodibenzofuran synthetic standard, having mass spectrum similar to "PBX" in pyrolysates.

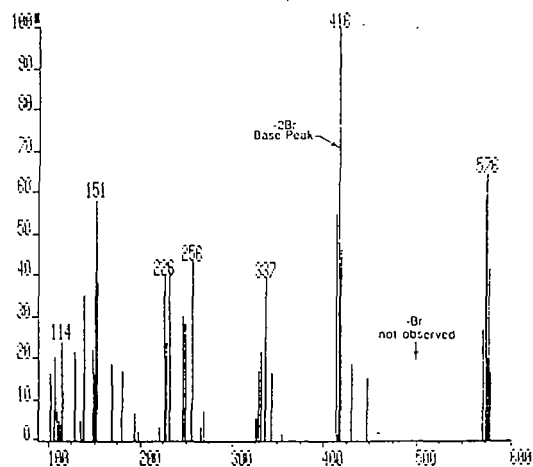


Figure 3. Methyl pentabromodibenzofuran synthetic standard, having mass spectrum differing from "PBX" in pyrolysates.

NOTICE

Although the research described in this article has been funded wholly or in part by the Environmental Protection Agency contract 68-03-3249 to Lockheed Engineering & Sciences Company, Inc, it has not been subject to the Agency's review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred. Mention of trade names or commercial products does not constitute an endorsement for use.

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