

CHROM. 12,949

## Note

### Gas chromatographic-mass spectrometric analysis of polybrominated biphenyl constituents of Firemaster FF-1

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(First received January 9th, 1980; revised manuscript received May 14th, 1980)

Sundstrom *et al.*<sup>1</sup>, De Kok *et al.*<sup>2</sup>, Jacobs *et al.*<sup>3</sup>, Dannan *et al.*<sup>4</sup> and Willett *et al.*<sup>5</sup> have all reported on the chromatographic characteristics of polybrominated biphenyls (PBBs); surprisingly little has been reported on the gas chromatographic-mass spectrometric (GC-MS) characteristics of the PBBs. Firemaster FF-1 was the principal contaminant in the food chain in the State of Michigan in 1973–1974<sup>6</sup>, and it has commonly been assumed that the PBBs alone were the primary toxic agents. We have had an opportunity to examine the GC-MS characteristics of a hexane extract of Firemaster FF-1 and have observed mixed polybromo- and chlorobiphenyls (PBCBs) as minor contaminants in addition to the well-known PBBs.

#### MATERIALS AND METHODS

Firemaster FF-1, lot No. FF1312-FT, was obtained from the National Institute of Environmental Health Sciences. A stock solution (1 mg/ml) in hexane was diluted for subsequent GC-MS analysis. A Finnigan 3200 gas chromatograph-quadrupole mass spectrometer with a 6100 data system was utilized in these studies. The GC-MS conditions were a column of 3% of SE-30 on Gas-Chrom Q (100–120 mesh) operated with a column temperature of 180°C, port and separator temperature 220°C, analyzer temperature 50°C and 100% helium (20 ml/min) as the carrier gas. The electron energy was 70 eV, and the mass spectrometer was calibrated by using perfluorotributylamine (FC43) from 34 to 614 *m/e*. The manufacturer<sup>7</sup> states that only masses up to 800 a.m.u. are accurately calibrated using FC43. Inasmuch as the heptabromobiphenyls (HpBBs) have a molecular weight of 706.3, this was deemed adequate for determining the major components of PBBs. Next, the high end of the mass spectrum was checked using bis(pentafluorophenyl)phenylphosphine, better known as decafluorotriphenylphosphine (DFTPP, Ultramark 433) as recommended by Eichelberger *et al.*<sup>8</sup>.

#### RESULTS AND DISCUSSION

The total ion chromatogram (TIC) of 1.5 µg of Firemaster FF-1 in hexane is illustrated in Fig. 1a. Peaks were labelled 0 through 10 and their retention times were

## PBB M62906

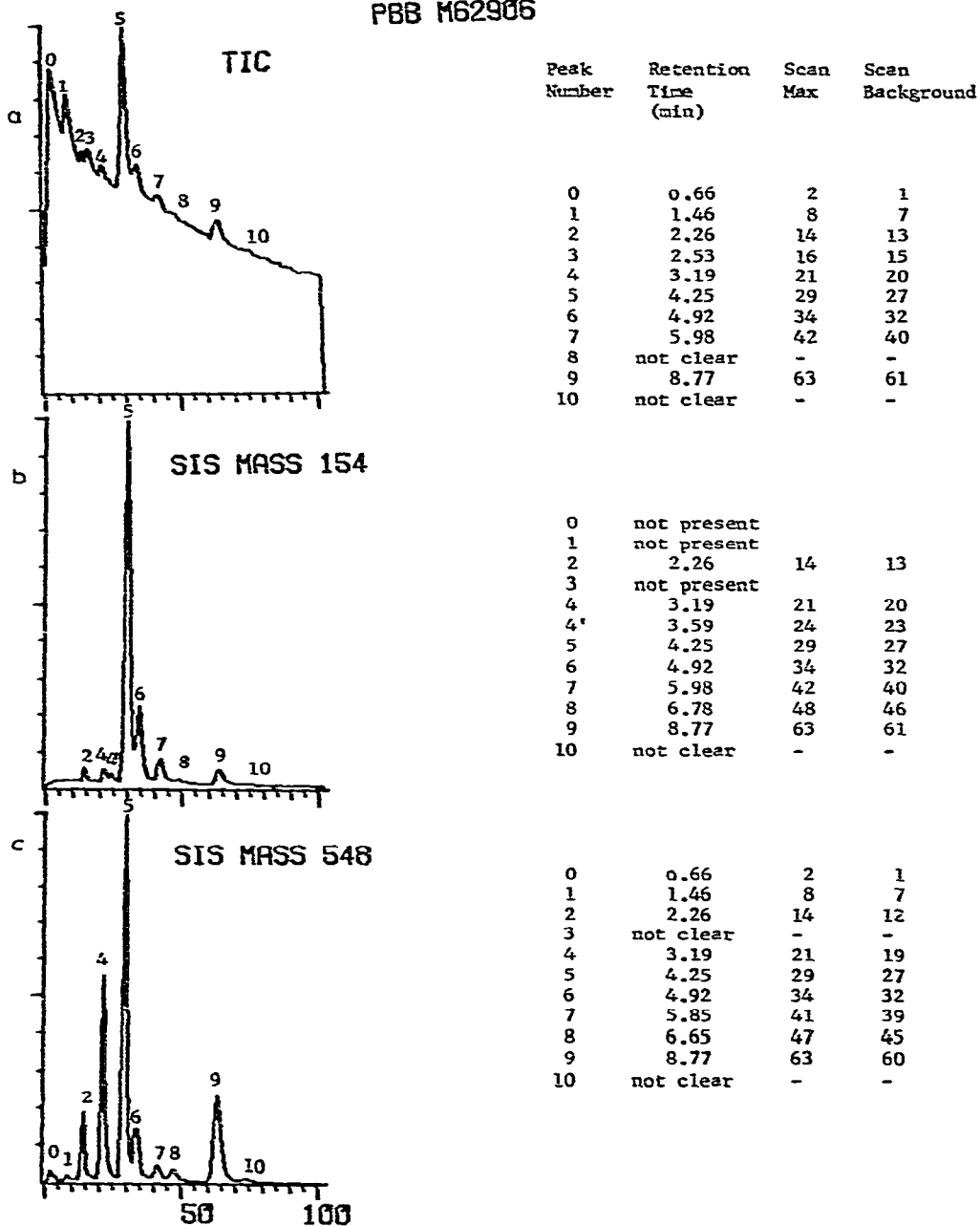


Fig. 1. Total ion chromatogram (TIC) and selected ion scans (SIS) of PBBs in Firemaster FF-1. The upper panel shows the TIC and the lower panels the SIS at  $m/e$  154 and 548. Peak numbers are as shown.

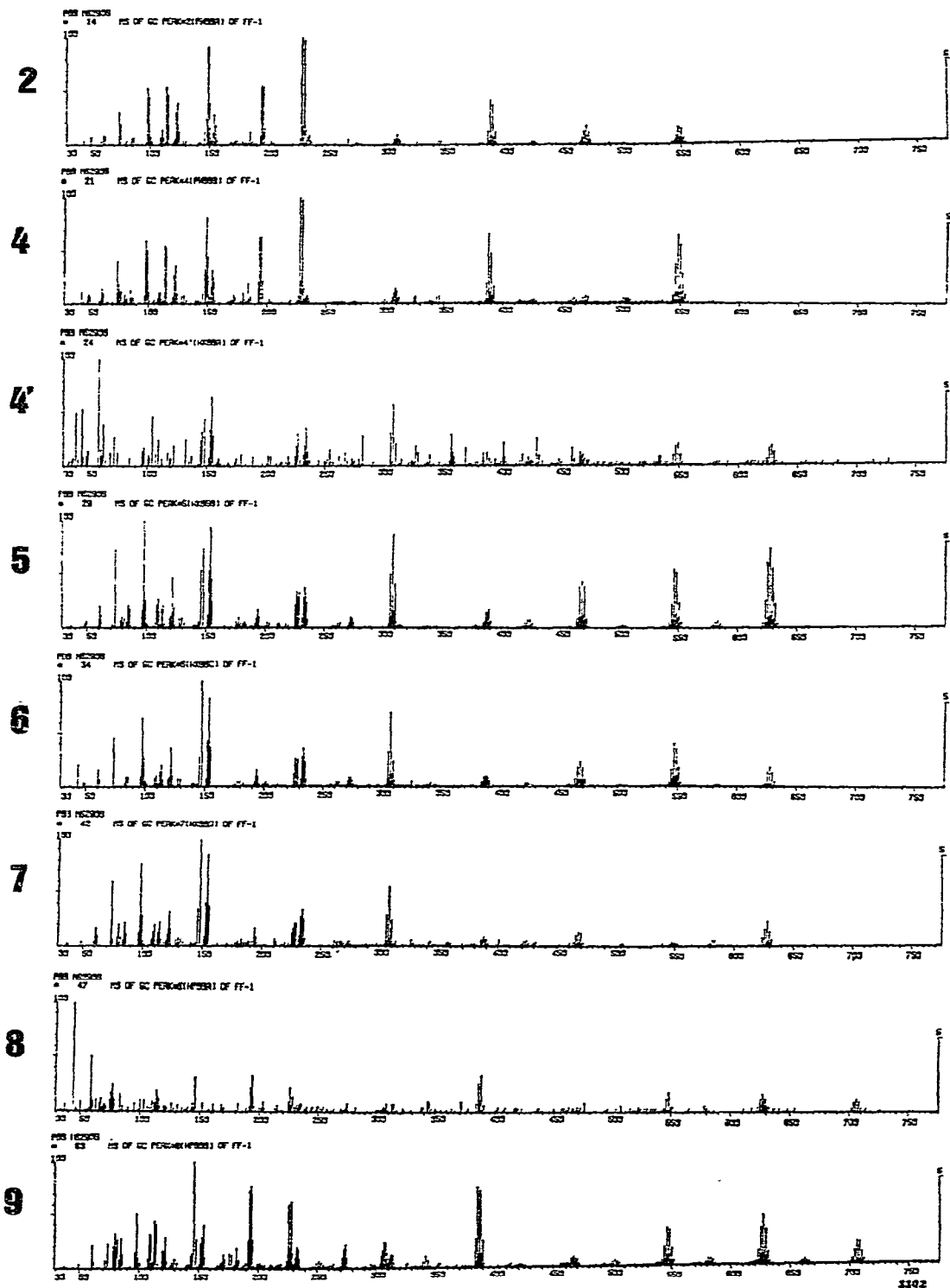


Fig. 2. Mass spectra of the major PBBs in Firemaster FF-1. The mass spectra of the major numbered peaks of the PBBs from Fig. 1 are shown. Note the presence of a chlorine contaminant in the PBBs. See text for details.

determined. Subsequently, selective ion scans for a.m.u. 98, 146, 147, 148, 149, 150, 154, 308, 547, 548 and 549 were carried out in order to better determine the retention times of ion fragments contained in PBBs, and to better define the specific compounds run as a TIC. The structures of the postulated positive-ion fragments were identified. Ions 154 and 548 were especially helpful, as shown in the selected ion scans (SIS) in Fig. 1b and 1c. The mass spectra for 8 of the 11 peaks are illustrated in Fig. 2. Peaks 0, 1, and 3 are possible unidentified contaminants. Peaks 2 and 4 are 2,2',4,5,5'-pentabromo-1,1'-biphenyl (PnBBa) and 2,3',4,4',5-pentabromo-1,1'-biphenyl (PnBBb), respectively. Peak 4' is a hexabromo-1,1'-biphenyl (HxBBa) whose bromine positions are yet to be assigned. Peak 5 is 2,2',4,4',5,5'-hexabromo-1,1'-biphenyl (HxBBb). Peak 6 is 2,2',3,4,4',5'-hexabromo-1,1'-biphenyl (HxBBc) and peak 7 is 2,3',4,4',5,5'-hexabromo-1,1'-biphenyl (HxBBd). The heptabromobiphenyls appear as peaks 8, 9 and 10, known as HpBBa,b, and c, respectively; HpBBb is 2,2',3,4,4',5,5'-heptabromo-1,1-biphenyl.

Typical molecular ions of the PBBs can be noted in the spectra in Fig. 2. For example, the lowest molecular ion  $x$  should be the sum of  $^{12}\text{C}$ ,  $^1\text{H}$  and  $^{79}\text{Br}$ , which, for HxBBb, is 622. The number of additional molecular ions is the sum of the bromines<sup>9</sup>. Especially interesting is that chlorine contaminants are observed in many of the PBBs. For example, HxBBb (peak 5) has the expected molecular ions (622, 624, 626, 628, 630, 632, and 634). The  $[\text{M} - ^{79}\text{Br}]$  groupings 543, 545, 547, 549, 551, and 553 a.m.u. are also observed. However, an unexpected set of ions (578, 580, 582, 584, 586, 588 and 590 a.m.u.) occurs in the spectrum of HxBBb. An enlargement of the  $[\text{M}]$  and  $[\text{M} - ^{79}\text{Br}]$  ions of peak 5 is shown in Fig. 3; similar analyses can be done for the other peaks. The analysis of relative abundances of the mass spectrum of peak 5 is consistent with a pentabromomonochlorobiphenyl contaminant that has a GC retention time similar to that of HxBBb. Capillary column separation of the various compounds in FF-1 is an essential task for the future. It can be observed in the mass spectra of Fig. 2 that many of the PBBs have minor chlorine contaminants. To our knowledge, we are

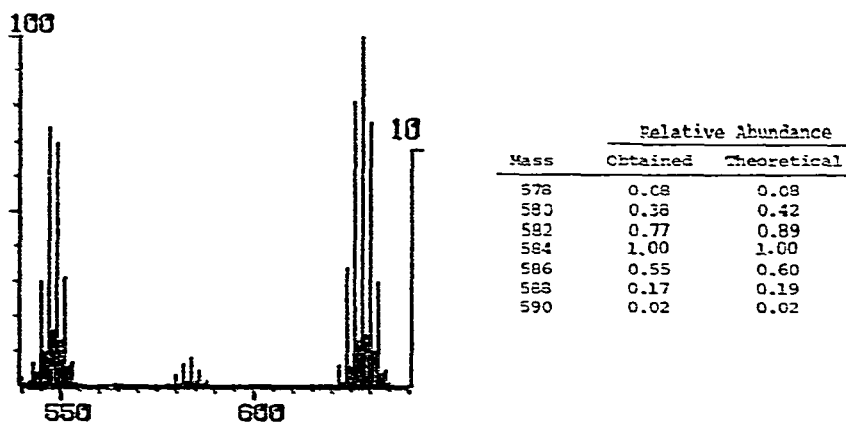


Fig. 3. Enlargement of the  $[\text{M}]$  and  $[\text{M} - ^{79}\text{Br}]$  molecular ion spectra of the major hexabromobiphenyl of Firemaster FF-1 indicating a pentabromomonochlorobiphenyl contaminant. Note that the obtained and theoretical abundances of the various molecular ions for a pentabromomonochlorobiphenyl contaminant are similar. The theoretical abundance for a  $\text{ClBr}_5$  compound was obtained from Beynon *et al.*<sup>9</sup> and calculated with mass 584 as 1.00.

the first to point this out, although it is certainly expected that minor amounts of chlorine will contaminate commercial bromine.

#### ACKNOWLEDGEMENTS

The authors would like to thank Mr. Benjamin Mathews for his assistance. This work was supported in part by a grant from the Michigan Department of Public Health and the Psychopharmacology Research Fund (S.E.D.).

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