

0.005). It is interesting that both dipeptides that contain hydroxyl groups, Pro-Hyp and Pro-Ser, had lower rate constants than Pro-Gly and Pro-Glu. Perhaps the lower rate constants for the dipeptides containing hydroxyl groups are due to competition of the hydroxyl groups with the imino nitrogen of Pro for the nitrosating agent.

Mirvish et al. (1973) has previously studied the nitrosation of Pro-Gly and reported a pH-dependent rate constant of $0.25 \text{ M}^{-2} \text{ s}^{-1}$. Our results for Pro-Gly are in excellent agreement with the previous report since we find a rate constant of $0.26 \text{ M}^{-2} \text{ s}^{-1}$. It is interesting to note that the pH-dependent rate constants for the four dipeptides N terminal in Pro examined in this study were substantially larger than the rate constant of $0.037 \text{ M}^{-2} \text{ s}^{-1}$ reported by Mirvish et al. (1973) for the free amino acid Pro. This of course suggests that the dipeptides would be expected to form N-nitroso derivatives in food, or in the stomach, more readily than Pro. Additional research will be required to determine whether nitrosated dipeptides N terminal in Pro form in food or in the stomach. Particularly pertinent to this question is a recent report by Ohshima and Bartsch (1981). These investigators reported that NPro, an N-nitroso compound that has not shown carcinogenic activity in experimental animals, can form

endogenously and is excreted quantitatively in the urine. Perhaps a reasonable approach in our future investigations would be to determine the urinary excretion products of nitrosated dipeptides that are N terminal in Pro.

Registry No. Pro-Gly, 2578-57-6; Pro-Glu, 67644-00-2; Pro-Hyp, 18684-24-7; Pro-Ser, 71835-80-8.

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Determination of Suspected Toxic Impurities in Firemaster FF-1 and Firemaster BP-6 by High-Resolution Gas Chromatography-High-Resolution Mass Spectrometry

Yves Tondeur, J. Ronald Hass,* Donald J. Harvan, Phillip W. Albro, and James D. McKinney

The analysis of Firemaster FF-1 (or BP-6) for minor and suspected toxic impurities has been accomplished by high-resolution GC-selected ion monitoring at medium and high resolution, the mass spectrometer being operated under a computer-controlled peak-matching system. Analysis for polybrominated naphthalenes reveals the presence of various components having an exact mass corresponding to the elemental compositions of tetra-, penta-, and hexabromonaphthalenes. The search for the corresponding polybrominated methylnaphthalenes or methylbromonaphthalenes results in a series of signals that have similar but incorrect exact masses. The analysis of the flame retardant mixture has also been extended to the measurement of the exact mass of some monochloropentabromobiphenyl isomers reported recently by Domino and Domino (1980) and to the screening for tetrabromobiphenylene isomers.

Firemaster FF-1 (or BP-6) is a complex mixture of highly brominated biphenyls that has been of environmental importance since the accidental contamination of animal feed in Michigan less than a decade ago (Kay, 1977). The presence of polybrominated aromatics other than the bromobiphenyls as trace impurities in the mixture has been the object of several studies and is of concern from a toxicological point of view (Taylor, 1979). Polybrominated naphthalenes, benzenes, and a possible methylbrominated furan have been reported by Hass et al. (1978). O'Keefe has independently reported polybrominated naphthalenes (O'Keefe, 1978, 1979). More recently, a monochloropentabromobiphenyl has been added to the list of detected impurities (Domino and Domino, 1980).

The chemical analysis of the flame retardant for these polybrominated aromatic contaminants has so far been limited to low-resolution characterization. We report here the results obtained for the direct screening of Firemaster (FF-1 or BP-6) by high-resolution gas chromatography (HRGC) at medium and high resolution of the mass spectrometer, MRMS and HRMS, respectively, the latter being under a computer-controlled peak-matching mode of operation (Harvan et al., 1982; Tondeur et al., 1983). The major advantage of this method is that it enables one to observe the peak profile of any signal falling in the preset mass window (typically selected to be twice the peak width at 5% peak height) scanned by the electric sector and, thereby, allowing the measurement of its exact mass. Application of this technique to the study of Firemaster FF-1 (or BP-6) for polybrominated naphthalenes, polybrominated methylnaphthalenes or methylbromonaphthalenes, monochloropentabromobiphenyls, and tetrabromobiphenylenes will illustrate its usefulness for the determination of minor components in complex mixtures.

National Institute of Environmental Health Sciences, Laboratory of Environmental Chemistry, Research Triangle Park, North Carolina 27709.

EXPERIMENTAL SECTION

Materials. Stock Firemaster solutions were prepared by dissolving the appropriate amount of solid in hexane (Burdick and Jackson, distilled in glass) in order to give a concentration of approximately $1 \mu\text{g}/\mu\text{L}$. The working solutions ($50 \text{ pg}/\mu\text{L}$ in hexane) were prepared from the concentrated ones ($100 \text{ ng}/\mu\text{L}$) made in toluene or in 10% tetrahydrofuran (THF) (Burdick and Jackson, distilled in glass) in hexane. The Firemaster samples studied were as follows: FF-1, lot no. FF-1312-FT, batch no. 03; FF-1, lot 7042; BP-6, Lansing, MI, and BP-6, Feb 14, 1974. The various standard compounds used in this study were synthesized previously (McKinney et al., 1981: i.e., 2,3,6,7-tetrabromonaphthalene; 1,2,4,6,7-pentabromonaphthalene; 1,2,3,5,6,7- and 1,2,3,4,6,7-hexabromonaphthalene isomers; 2-methylpentabromonaphthalene (synthesis adapted from previous work). A 5% benzene (Burdick and Jackson, distilled in glass) in hexane mixture was used to prepare the stock solution of 2,3,6,7-tetrabromobiphenylene.

Methods. Gas Chromatography-Mass Spectrometry (GC-MS). Gas chromatography was performed on a Hewlett-Packard Model 5700 gas chromatograph using either an SE-30 or OV-1 fused silica capillary column (0.32 mm o.d. \times 25 m; J. and W. Scientific) that was directly coupled to the ion source of the mass spectrometer. Typically, $1 \mu\text{L}$ of solution was injected onto a cold column. Following the elution of the solvent, the column was ballistically heated to 150°C and then programmed at $8^\circ\text{C}/\text{min}$ to 250°C . The mass spectrometer (VG Micromass ZAB-2F coupled to a Finnigan-Incos 2300 data system) was operated in the electron impact (EI) mode with an electron energy of 70 eV, the accelerating voltage for the transmission of the lock mass ions being kept at 8 kV. The interface and source temperatures were held at 250°C . All the relative retention times (RRT) are given relative to that of the major hexabromobiphenyl isomer in FF-1 (peak D) (2,4,5,2',4',5'-hexabromobiphenyl).

Selected Ion Monitoring (SIM). The detailed description of the mode of operation of the computer-controlled peak-matching unit is reported elsewhere (Harvan et al., 1982). A VG Micromass ZAB-2F mass spectrometer and a digital multiple ion detector unit (DIGMID) were used for acquisition of the data. The DIGMID unit enables peak matching of up to seven ions with respect to a reference compound.

The resolution of the mass spectrometer was set either at 5000 or at 10000 (5KRP or 10KRP) using the 5% crossover definition, and the width of the mass window scanned by the electric sector was 400 and 200 ppm, respectively. The lock mass ions were usually a PFK ion or an ion from C_2I_4 . The exact masses of the monitored ions were m/z 441.7029, 443.7009, and 445.6989 for tetrabromonaphthalene, m/z 457.7166 for tetrabromomethylnaphthalene, m/z 521.6115, 523.6095, and 525.6075 for pentabromonaphthalene; m/z 535.6271 for methylpentabromonaphthalene, m/z 583.5862 for monochloropentabromobiphenyl, m/z 599.5220, 601.5201, and 603.5181 for hexabromonaphthalene, m/z 615.5357 for methylhexabromonaphthalene, and m/z 465.7029, 467.7009, and 469.6989 for tetrabromobiphenylene. The sampling rate was 0.5 s/peak. When desired, ions for penta- (m/z 549.6252) and hexabromobiphenyls (m/z 627.5357) were sampled in 0.2 s each.

RESULTS AND DISCUSSION

Figure 1 represents the reconstructed ion chromatogram of Firemaster FF-1 obtained by full-scan GC-MS in the EI mode of ionization. The early eluting components, some barely seen on the total ion current (TIC) were identified

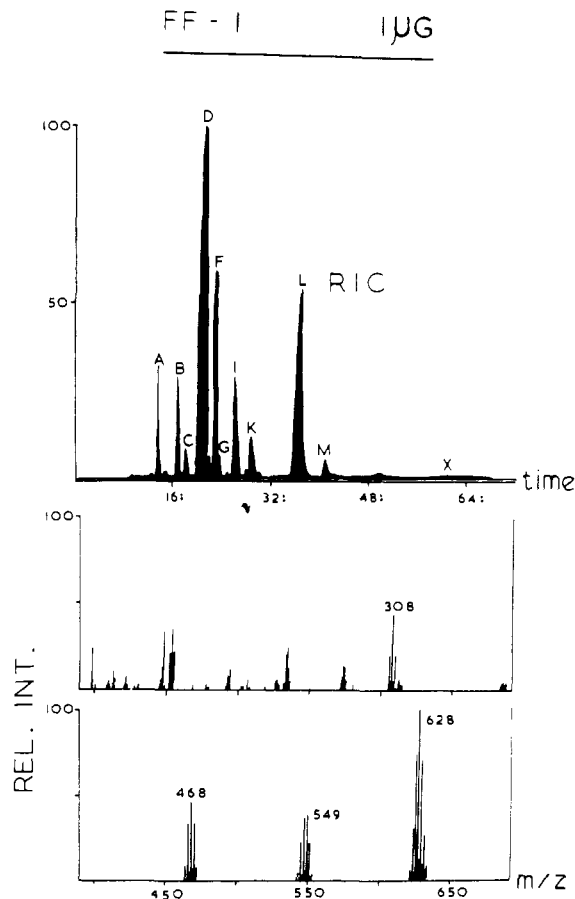


Figure 1. Reconstructed ion chromatogram of a capillary GC run of Firemaster FF-1 ($1 \mu\text{g}$) and the mass spectrum of the major component (peak D; hexabromobiphenyl) (EI; fused silica OV-1, 20 m, was programmed from 150 to 250°C at $8^\circ\text{C}/\text{min}$).

as tetra- and pentabromobiphenyl isomers while the later eluting ones were assigned as hepta- and octabromobiphenyls. The majority of the GC peaks are due to the hexabromobiphenyl isomers, which constitute the bulk of the mixture. Also, the figure displays the mass spectrum of the main component, 2,2',4,4',5,5'-hexabromobiphenyl. A list of the various polybrominated biphenyls characterized in the mixture and their relative retention times (RRT) is in Table I.

Dynamically Recorded High-Resolution Selected Ion Monitoring. As a compromise between sensitivity and specificity for the selected ion monitoring method, an approach was used in which the actual peak profile of the signal can be recorded, stored, and retrieved for exact mass determination. The principles of operation and an estimation of the accuracy and precision of the method are reported elsewhere (Harvan et al., 1982; Tondeur et al., 1983). Briefly, the mass window sampled was bracketed by two pulses and its width was chosen to be twice the peak width at 5% height. The center of this window scanned by the electric sector corresponds to the exact mass of the monitored ions. As Figure 1 illustrates, one can readily take advantage of both the separation power of a capillary GC column and the resolving power of the mass spectrometer. Figure 2 shows the peak profiles obtained for selected ions characteristic of three closely eluting analytes as a function of the individual scans taken as the components elute from the GC.

Tetrabromobiphenylenes. The electron impact mass spectrum of 2,3,6,7-tetrabromobiphenylene has as its base peak the molecular ions (m/z 464, Br_4) and an intense peak for the loss of Br_2 . This particular isomer has an RRT of

Table I. Relative Retention Times (RRT) of the Various Polybrominated Biphenyl Isomers Found in Firemaster FF-1 by GC-MS (See Figure 1)

no. of bromines, <i>n</i>	RRT	peak labels
4	0.54	
4	0.63	
5	0.66	
5	0.71	A
5	0.74	
5	0.76	
5	0.83	B
6	0.88	C
6	1.00 ^a	D
6	1.01	E
6	1.06	F
6	1.08	G
6	1.14	H
6	1.20	I
7	1.25	J
7	1.30	K
7	1.34	
7	1.59	L
7	1.75	M
7	1.85	
7	2.08	
8	2.23	

^a This signal corresponds to the major component of FF-1, i.e., 2,4,5,2',4',5'-hexabromobiphenyl taken as the reference compound for calculation of the RRT.

0.80; thus, it elutes just before the major components of the flame retardant mixture (Table I). However, as can be seen from the data reported in Table II and from Figure 3, an interference in the tetrabromonaphthlene measurement (peak * in Table II) due to a minor coeluting hexa-

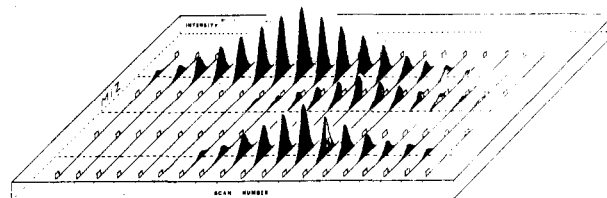


Figure 2. Dynamically recorded high-resolution-selected ion monitoring representation of the peak profiles for selected ions characteristic of three closely eluting components as a function of the scan number. Each sampled mass window is bracketed by two pulses.

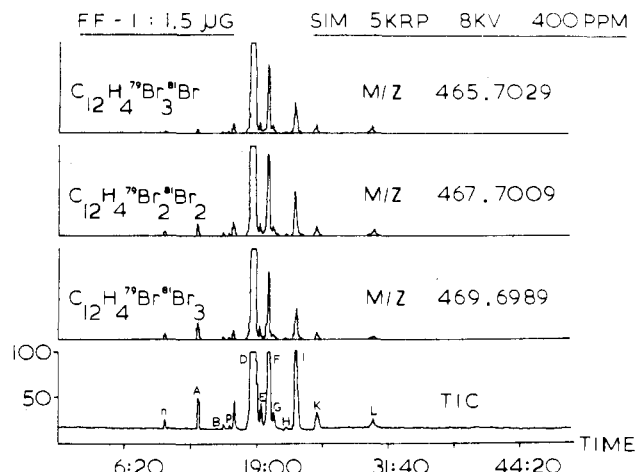


Figure 3. Selected ion chromatograms and total ion current traces obtained from the analysis of 1.5 µg of Firemaster FF-1 on a capillary column while monitoring three ions of the tetrabromobiphenylene molecular ion cluster.

Table II. Exact Mass Measurements Obtained by High-Resolution Selected Ion Monitoring of Firemaster FF-1^b

RRT	peak labels	exact masses, ppm, from				
		$C_{12}H_4^{79}Br_3^{81}Br$, <i>m/z</i> 465.7029, Br ₄ -biphenylene	$C_{12}H_4^{79}Br_2^{81}Br_2$, <i>m/z</i> 467.700, Br ₄ -biphenylene	$C_{12}H_4^{79}Br^{81}Br_3$, <i>m/z</i> 469.6989, Br ₄ -biphenylene	$C_{12}H_5^{79}Br_2^{81}Br_3$, <i>m/z</i> 549.6256, Br ₃ -biphenyl	$C_{12}H_4^{79}Br_3^{81}Br_3$, <i>m/z</i> 627.5357, Br ₆ -biphenyl
0.53	n	+28	+34	+35	NS	NS
0.56		+35	+34	+38		
0.57		+38	+32	+36	NS	NS
0.63		+21	+36	+33		
0.65		+20	+27	+26	+26	NS
0.70	A	+18	+26	+28	+37	NS
0.72		+23	+31	+28	+9	NS
0.74		+31	+24	+23	+11	NS
0.76		weak	+28	+25	+9	NS
0.77			+8	+9	+9	NS
0.80	* ^a	-5	+3	+8	-7	+7
0.83	B	+8	+19	+25	+18	NS
0.86	p	-3	0	+2	+7	+9
0.88	C	-2	+2	+2	+7	+13
0.91			-1		+9	+6
1.00	D	-2	+2	+5	+6	+9
1.01	E	-2	+5	+2		
1.06	F	-2	+4	+7	+4	+15
1.08	G	-3	+7	+3		
1.14	H	-5	0	0		
1.19	I	-3	+1	+2	0	+13
1.30	K	-8	-1	0	-15	+13
1.59	L	-29	-17	-11	-18	+7
1.74		-23	-13	-5	-18	+4
2.09		-20	-15	-13	-26	+7
2.14		-44	-15	+8		
2.22		-49	-37	weak	-10	-10
2.25		-42	-34	-18	weak	-4

^a This signal has the same RRT as 2,3,6,7-tetrabromobiphenylene. ^b The measured values are given in ppm from the theoretical ones (5KRP; 400-ppm mass window sampled for each of the indicated ions). The RRT are relative to that of the major hexabromobiphenyl isomer (peak D; see Figures 1 and 3). The symbol NS means that no signal was detected in that channel.

Table III. Exact Mass Measurements of the GC-MS Signal Labeled H in Firemaster FF-1 Obtained by High-Resolution Selected Ion Monitoring at 5KRP and 10KRP (BrNp = Bromonaphthalene; Std = Standard)

sample	MS resolving power	mass window, ppm	exact mass, Δ , ppm, from		
			$C_{10}H_2^{79}Br_4^{81}Br_2$, Br ₆ Np, <i>m/z</i> 559.5220	$C_{10}H_2^{79}Br_3^{81}Br_3$, Br ₆ Np, <i>m/z</i> 601.5201	$C_{10}H_2^{79}Br_2^{81}Br_4$, Br ₆ Np, <i>m/z</i> 603.5181
50 pg of Br ₆ Np std	5 000	400		0	
1.5 μ g of FF-1 or BP-6	5 000	400		+9	
mixture of 50 pg of Br ₆ Np and 0.9 μ g of FF-1	5 000	400		+2 (std) -2 (FF-1)	
50 pg of Br ₆ Np std	10 000	200		+4	
1.5 μ g of FF-1	10 000	200		+6	
50 pg of Br ₆ Np std	10 000	200	+2	-2	+2
1.5 μ g of FF-1	10 000	200	0	+2	-1

bromobiphenyl isomer is observed, which makes the direct analysis difficult. The peak labels in Table II assigned to the major components correspond to Figures 1 and 3. The results demonstrate the good agreement between the measured exact masses and the theoretical values when direct comparison with the GC-MS full-scan data of FF-1 is possible. For instance, a tetrabromobiphenyl molecular ion ($C_{12}H_6^{79}Br_3^{81}Br$) is expected to be 38 ppm (18 mmu) higher in mass than the monitored ion for tetrabromobiphenylene ($C_{12}H_5^{79}Br_2^{81}Br_2$) (see peak n, Table II and Figures 3 and 4a). Another example is provided by the loss of a bromine radical from the pentabromobiphenyl ion (peak A, Table II and Figure 4b), which results in the formation of a fragment ion ($^{13}CC_{11}H_5^{79}Br_3^{81}Br$) calculated to be 28 ppm (13 mmu) higher in mass than for $C_{12}H_4Br_4$. Finally, a hexabromobiphenyl (see peaks C-I, Table II and Figure 4c) losing Br_2 gives an ion having the same elemental composition as tetrabromobiphenylene. Any improvement in sensitivity in the analysis for this compound thus requires a better GC separation or sample fractionation prior to analysis. [For the 2,3,6,7-tetrabromobiphenylene isomer, none was detected at the limit of detection that is estimated to be 30 ppm on a DB-5 fused silica column (25 m).]

Polybrominated Naphthalenes. Firemaster FF-1 (or BP-6) has been analyzed by GC-MS/SIM for tetrapenta- and hexabromonaphthalene isomers. The results of our investigation revealed the presence of one component having an exact mass of a hexabromonaphthalene (Table III). The exact mass measurements obtained either at 5000 or at 10000 resolution are consistent and within the experimental error of the theoretical value. The coinjection of 50 pg of 1,2,3,5,6,7-hexabromonaphthalene standard (RRT = 1.18) with 0.9 μ g of FF-1 gives two signals in the hexabromonaphthalene channel: one for the reference compound with a signal/noise ratio (S/N) >50 and one from Firemaster itself (RRT of 1.14, the same retention time as that of component H of Table I), both of which are measured within 1 mmu of the monitored mass. (The isotopic ratios, based on area measurements, support the postulation of the presence of a component with an elemental composition of $C_{10}H_2Br_6$ [(M + 4)/(M + 6) = 0.8 (theoretical) and 0.6 (experimental); (M + 4)/(M + 8) = 1.0 (theoretical) and 0.8 (experimental); (M + 6)/(M + 8) = 1.3 (theoretical) and 1.3 (experimental)].) Semiquantitative data are obtained by using the 1,2,3,4,6,7-hexabromonaphthalene isomer as an external calibrant; concentration of this component in Firemaster is estimated to be approximately 150 ppm.

Two other components (out of a total of 11) in the mixture were found to have an exact mass, within the experimental error, corresponding to the elemental composition of pentabromonaphthalene, $C_{10}H_3Br_5$. The com-

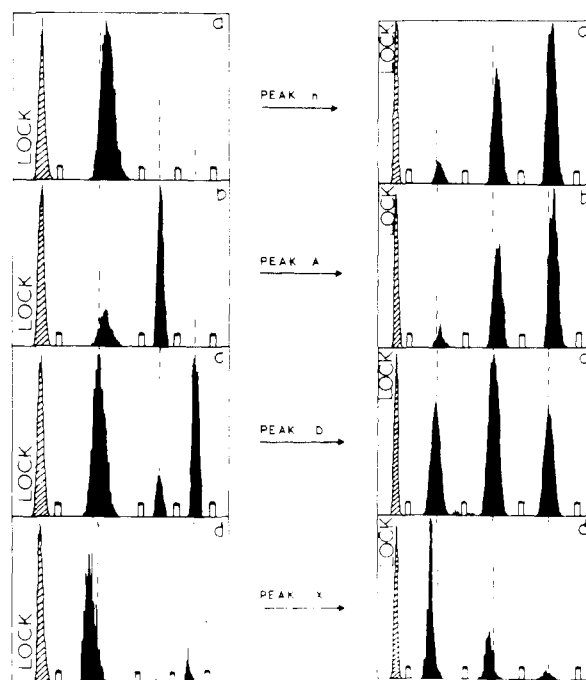


Figure 4. Peak profiles of four GC-MS signals obtained after analysis of Firemaster FF-1 by HRGC-HRMS (see Figure 3 for the peak labels). The first series of peak profiles (left) are obtained by monitoring consecutively one major ion for tetrabromobiphenylene ($M + 2$; with a dwell time of 0.5 s) and penta- (M^+ ; with a dwell time of 0.2) and hexabromobiphenyl (M^+ ; with a dwell time of 0.2 s). On the right, three major ions for tetrabromobiphenylene (M ; $M + 2$; $M + 4$) are monitored.

ponent having RRT of 1.14 was measured to be 4–6 ppm lower in mass than the theoretical value (i.e., within experimental error of the theoretical m/z for this elemental composition) and was due to a fragment ion of the previously described hexabromonaphthalene component since the ^{13}C fragment ion of $C_{10}H_2Br_5^+$ is 4.5 mmu (9 ppm) lower in mass than that of $C_{10}H_3Br_5$. This value of -9 ppm is actually the one measured when a hexabromonaphthalene standard is analyzed. The earlier eluting of these two positive signals was measured to be within 2 ppm from the calculated value for $C_{10}H_3Br_5$, and its RRT of 0.72 corresponds to the RRT of the 1,2,4,6,7-pentabromonaphthalene standard.

Finally, only one of the 18 signals (peak B from Table IV) observed while monitoring for tetrabromonaphthalenes has been found to possess an exact mass corresponding to $C_{10}H_4Br_4$ (tetrabromonaphthalene). Its RRT of 0.83 is higher than the value of the symmetrical 2,3,6,7-tetrabromonaphthalene isomer used as a reference. Examination of Table IV shows that the majority of the observed

Table IV. Exact Mass Measurements Obtained by HRGC-HRMS while Monitoring for Tetrabromonaphthalene Isomers (5KRP; 400-ppm Mass Window) in FF-1^c

RRT	exact mass difference in ppm from $C_{10}H_4^{79}Br_9^{81}Br_2$ (Br_4Np), m/z 443.7009	
	1.5 μ g of FF-1	1.5 μ g of FF-1 (or BP-6) plus 50 pg of 2,3,6,7 Br_4Np
0.59		-5 ^a
0.71	(-25)	(-15) ^b
0.83 (B)	-11	-7
	(-28)	
0.88	-46	-39
1.00	-26	-30
1.01	-37	-55
	(-33)	
1.06	-38	-41
1.08	-35	-44
1.14	-42	-32
1.20 (I)	-38	-37
1.25	-38	
1.30	-46	-41
	(-25)	
	(-26)	
1.59	-41	-36
	(-51)	
1.75	(-41)	-41

^a The values in the second row are obtained from the run of FF-1 fortified with 30 ppm of 2,3,6,7-tetrabromonaphthalene. ^b The measurements performed on weak signals are given in parentheses. ^c Under these conditions, 2,3,6,7-tetrabromonaphthalene gave a RRT of 0.59 and an exact mass difference of -5 ppm.

signals may have their origin in the loss of a $C_2H_2Br_2$ fragment from the hexabromobiphenyl isomers resulting in the formation of an ion 40 ppm lower in mass than the monitored one. This fragmentation reaction is not observed in a normal electron impact spectrum of hexabromobiphenyl since peaks of <0.1% are not normally recorded. Component H from Table IV is a composite signal; one part is due to the loss of $C_2H_2Br_2$ from a hexabromobiphenyl and one due to the loss of Br_2 from the probable hexabromonaphthalene. This leads to the formation of an identical ion 40 ppm lower in mass than m/z 443.7009 ($C_{10}H_4Br_2Br_2$). The contribution of the weak signal I (see Table IV) due to the loss of Br from $C_{10}H_3Br_5$ is obscured by the larger signal originating from a coeluting hexabromobiphenyl isomer.

The positive response observed for B is actually due to an interference from the ion formed by the loss of a bromine radical from pentabromonaphthalene. The ¹³C-containing isotope of this fragment ion is expected to be mass shifted by -10 ppm from $C_{10}H_4Br_4$. The relative intensities of the $M + 2$, $M + 4$, and $M + 6$ ions for this signal B in FF-1 are 1.5:2:1, and for 50 pg of reference compound, one gets 1.2:1.9:1 compared to the theoretical values of 1.0:1.5:1.

Polybrominated Methyl-naphthalenes or Methyl-bromonaphthalenes. The search for polybrominated methyl- or bromomethyl-naphthalenes in Firemaster FF-1 shows that none of the seven signals measured for the pentabromo isomers gives the proper exact mass; they are about 25 ppm (13 mmu) higher in mass than $C_{11}H_5Br_3Br_2$

(m/z 535.6271). Under the same conditions, the reference compound (50 pg; S/N ~ 45) is measured within 2 ppm of the theoretical exact mass. The data recorded at 5000 and at 10000 resolution are consistent. The reference compound has a relative retention time of 0.94 and the relative retention times of the seven signals range from 0.75 to 0.94.

A broad GC peak with a RRT of 1.20 is observed when monitoring for the hexabromo isomer. This signal is found to be 30 ppm higher in mass than the one monitored. No attempt was made to assign an elemental formula to this ion.

Thirteen weak signals were measured for the methyl-tetrabromonaphthalenes and about half of them were within -2 to +14 ppm of the monitored ion $C_{11}H_6Br_2Br_2$ at m/z 457.7166 (5KRP). The RRT of these signals range from 0.66 to 1.41. The lack of standard compound restricts us from any further comments.

Monochloropentabromobiphenyls. Three major signals responding to $C_{12}H_4Cl^{79}Br_2^{81}Br_3$ are observed in FF-1. Their exact masses at 10000 resolving power are measured to be 7, -3, and -4 ppm from the monitored ion, which is within experimental error of the theoretical value. Their relative retention times are 0.83, 0.88, and 0.98. These results support the earlier findings of Domino and Domino (1980) at low mass spectrometric resolution.

CONCLUSION

Dynamically recorded high-resolution selected ion monitoring coupled to a high-resolution gas chromatographic column can provide specific information regarding trace impurities in a complex mixture such as Firemaster FF-1 and BP-6. Several examples of interfering isobaric ions close to the elemental composition of the studied compounds described in this work demonstrate the importance of recording the peak profile data while sweeping over a small mass window. However, even though this technique introduces a new dimension in specific characterization, it does not constitute an unambiguous identification of polybrominated aromatics for which appropriate standards are not available.

ACKNOWLEDGMENT

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Registry No. Br_4Np , 88703-31-5; Br_5Np , 56448-55-6; Br_6Np , 56480-06-9; 2,2',4,4',5,5'-hexabromobiphenyl, 59080-40-9; 2,2',3,4,4',5,5'-heptabromobiphenyl, 67733-52-2; Firemaster FF-1, 67774-32-7; Firemaster BP-6, 59536-65-1; monochloropentabromobiphenyl, 88703-30-4.

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