

## APGC-MS/MS Investigation of a Complex Mixture of Polyhalogenated Dioxins and Furans (PXDD/Fs) Generated in Fire Debris

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### APPLICATION BENEFITS

Using atmospheric pressure gas chromatography in combination with triple quadrupole mass spectrometry provides:

- Highly sensitive analysis for trace level components in a complex sample matrix.
- Increased ease-of-use and sensitivity over the more traditionally used magnetic sector instruments.
- Selectivity of the PXDD/F isomers from similar persistent organic compounds in the matrix.
- Understanding the level of exposure of first responders, especially fire fighters, to potentially toxic dioxins and furans that are currently unregulated.

### WATERS SOLUTIONS

[Atmospheric Pressure Gas Chromatography \(APGC\)](#)

[Xevo® TQ-S](#)

[MassLynx® MS Software](#)

### KEYWORDS

Dibenzo-p-dioxin, Dibenzofuran, PXDD, PXDF, mixed halogen, APGC, Atmospheric Pressure Gas Chromatography, TQ-S

### INTRODUCTION

In the 15 years following the September 11th attacks on the World Trade Center, studies have revealed an overwhelming increase of 19% in the total cancer rates of firefighters exposed to the WTC debris.<sup>1</sup> Separate studies have also uncovered an overall increase in cancer rates of firefighters when compared to the general population.<sup>2</sup> First responders exposed to fire debris, either during an active fire or after the flames have been extinguished are exposed to a very complex mixture of compounds, including some potentially toxic compounds. Some of these compounds are combustion byproducts of flame retardants present in the materials burning in the fire.

Among some of the most used flame retardants are the brominated flame retardants (BFRs), specifically polybrominated diphenyl ethers (PBDEs). Although some PBDE formulations are being phased out of use, not all have been replaced and many consumer products in use still contain PBDEs. Studies have determined that when combusted, PBDEs create the dibenzo-p-dioxin and dibenzofuran backbones, substituted with halogens (Br and/or Cl) present in the combusted materials.<sup>3-4</sup>

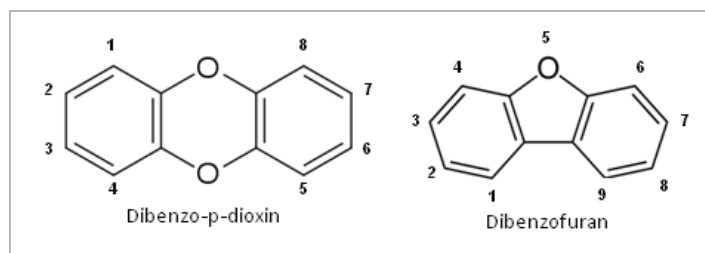


Figure 1. Structures of dibenzo-p-dioxin and dibenzofuran backbone. Halogen substitution can occur at any of the open numbered positions.

Currently, only 17 chlorinated dioxins and furans (PCDD/Fs) are regulated and routinely monitored. These monitoring methods exclude the polybrominated (PBDD/Fs) and mixed bromo-chloro (PXDD/Fs) congeners. Toxicities of the PBDD/Fs and PXDD/Fs may be equivalent or even exceed that of the most toxic PCDD/Fs, specifically 2,3,7,8-TCDD. Therefore, the potential toxicity of samples may not be fully represented using current regulations.

Traditionally, dioxin analysis is performed using a magnetic sector instrument that utilizes electron impact (EI) gas chromatography. However, in order to take advantage of the sensitivity the magnetic sector offers, only a limited number of compounds can be targeted in a single run. To be able to target the possible thousands of dioxin and furan congeners that can be formed, a tandem quadrupole mass spectrometer can be used. Waters® Xevo TQ-S is capable of maintaining the sensitivity and scanning speed needed to cover the wide range of MRM transitions required for this analysis.

Additionally, the emergence of softer ionization techniques, such as APGC, in combination with time-of-flight or tandem quadrupole mass spectrometry (APGC-MS/MS) has been shown to be selective and sensitive enough to enable routine analysis of these compounds.

In this application note, we focus on the combination of APGC coupled to a Xevo TQ-S tandem quadrupole instrument to better characterize the extent of dioxin and furan generation (polybromo- and mixed halogenated) in simulation fire debris in order to gain a better understanding of the levels of these compounds that first responders are exposed to.

## EXPERIMENTAL

### Sample preparation

Fire debris samples were generated at the Fire and Emergency Services Training Institute (FESTI) in Toronto, Ontario, Canada. Both a household fire (consisting of household furniture) and an electronics fire (consisting of electronics typically contained in an office) were simulated. Multiple samples from different locations in the fire debris were collected after the fires were extinguished. Samples collected included pieces of debris and ash, as well as wipes taken from the walls of the burn cell and firefighter equipment. Samples were extracted at The Pennsylvania State University using the Ontario Ministry of Environment and Climate Change (MOECC) method E3418.<sup>5</sup> Briefly, samples were extracted in hexane over a 24 hr period using a Soxhlet apparatus. Prior to extraction, the samples were fortified with a mixture of <sup>13</sup>C labeled internal standards (Table 1). Following extraction, samples were concentrated and subjected to a two-stage column cleanup process: (a) acid-base silica (b) 5% carbon/silica (w/w). Prior to injection on the APGC-MS/MS, the extracts were concentrated to 100 µL using a rotary evaporator.

Table 1. List of the <sup>13</sup>C labeled internal standards fortified into fire debris samples prior to extraction.

Dibenzofurans	Dibenzo-p-dioxins
<sup>13</sup> C <sub>12</sub> -2,3,7,8-tetrachloro	<sup>13</sup> C <sub>12</sub> -2,3,7,8-tetrachloro
<sup>13</sup> C <sub>12</sub> -3-bromo-2,7,8-trichloro	
<sup>13</sup> C <sub>12</sub> -2,3-dibromo-7,8-dichloro	<sup>13</sup> C-2,3-dibromo-7,8-dichloro
	<sup>13</sup> C <sub>12</sub> -2,3,7,8-tetrabromo
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-pentachloro	<sup>13</sup> C <sub>12</sub> -1,2,3,7,8-pentachloro
<sup>13</sup> C <sub>12</sub> -2,3,4,7,8-pentachloro	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-hexachloro	<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8-hexachloro
<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-hexachloro	<sup>13</sup> C <sub>12</sub> -1,2,3,6,7,8-hexachloro
<sup>13</sup> C <sub>12</sub> -1,2,3,7,8,9-hexachloro	
<sup>13</sup> C <sub>12</sub> -2,3,4,6,7,8-hexachloro	
<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-heptachloro	<sup>13</sup> C <sub>12</sub> -1,2,3,4,6,7,8-heptachloro
<sup>13</sup> C <sub>12</sub> -1,2,3,4,7,8,9-heptachloro	
	<sup>13</sup> C <sub>12</sub> -octachloro

A variety of MRM transitions were monitored for each PXDD, PXDF, PBDD, and PBDF congener class (3 to 6 transitions each). Two separate methods were created, with the PXDD and PXDF compounds in one method, and the PBDD and PBDF compounds in a separate method. The PXDD/F method contained approximately 150 total MRM transitions monitoring 40 different native and labeled groups of congeners, while the PBDD/F method had approximately 50 MRM transitions monitoring 17 different congener groups. Complete MRM information for all of the compounds is detailed in the Appendix. The method information can also be found in the APGC Quanpedia™ database.

#### APGC conditions

Column:	60 m x 0.18 mm x 0.10 µm Rtx Dioxin-2 1.0 m x 0.32 mm stainless steel Sulfinert tubing coupled to column exit through transfer line
Carrier gas:	Helium
Injection mode:	Splitless
Injector liner:	4.0 mm drilled hole Uniliner
Injector temp.:	290 °C
Injection volume:	0.5 µL
Flow rate:	1.1 mL/min
Oven program:	120 °C for 1 min 35 °C/min to 200 °C 4.5 °C/min to 280 °C, hold 8 min 20 °C/min to 330 °C/min, hold 15 min

#### MS conditions

MS system:	Xevo TQ-S
Ionization mode:	APGC positive ion mode
Ionization mechanism:	Charge transfer (dry)
Source temp.:	150 °C
Auxiliary gas:	400 L/h
Collision gas:	0.18 mL/min
Cone gas:	Off for first 8 min of run 215 L/h for rest of run
Corona current:	20 µA for first 8 min of run 4.0 µA for rest of run
Transfer line temp.:	360 °C

## RESULTS AND DISCUSSION

### MRM METHOD DEVELOPMENT

Due to only a handful of PXDD/F standards being commercially available, MRMs were developed for a wide range of PXDD/F congeners using a previously characterized fire debris sample. Dioxin and furan molecules are known to preferentially lose a -COX (X = Br or Cl) fragment, while -COBr occurs more readily than -COCl when a mix of halogens are present on the DD or DF backbone. Therefore, this fragment was chosen for all compounds using the most abundant mass in the molecular ion cluster (M+2 or M+4) as the parent ion. The second transition selected for all compounds utilized the second most abundant molecular ion losing the COBr group. A variety of other fragments were used to develop other MRMs as well, as described in the Appendix.

### IDENTIFICATION OF MIXED HALOGEN DIOXINS AND FURANS IN FIRE DEBRIS SAMPLES

Due to the enhanced sensitivity of the Xevo TQ-S, a large variety of PXDF congener groups were identified in both the household and electronics fire debris samples. The fire debris generated in the electronics fire contained the largest variety and highest concentrations of PXDFs. This is expected due to the large quantity of the types of flame retardants typically present in electronics products. Within each group of congeners identified in the samples a large number of potential isomers were observed, as shown in Figure 2. Each peak in Figure 2 represents an isomer of the Br<sub>2</sub>Cl substitution pattern and as expected, the peaks were not fully resolved due to the immense complexity resulting from the large number of possible isomers created in the fire. Individual PXDD/Fs were generated in the samples in the parts per trillion (ppt) to parts per billion (ppb) range, so the additional sensitivity of the Xevo TQ-S is required to detect most of the compounds. Figure 2 also demonstrates the calculated signal-to-noise values for a selection of the peaks, ranging from 12 to 89.

Using a set of 13C labeled internal standards (Table 1), semi quantification of the identified PXDFs was performed. Semi quantification was performed because internal standards for every congener are not commercially available. As a result of the complexity of the chromatograms collected, quantification was performed as the sum of all of the individual peak areas comprising one congener group. For example, all peaks in Figure 2 were summed together and treated as one peak area. Table 2 summarizes the concentration ranges calculated in the samples collected from each fire simulation.

The concentrations varied greatly among the samples.

From the household fire, particulate debris scraped from the door of the burn cell contained the highest concentrations of PXDFs. In the electronics fire, the highest concentrations of PXDFs were actually collected from a firefighter's helmet. These results seem to suggest that the polyhalogenated furans are more likely to partition into airborne particulate matter than to remain in the debris itself. The electronics fire debris also contained PXDDs in some of the samples. The PXDDs were at much lower concentrations than the PXDFs, and fewer congeners were identified. Among the dioxins identified were BrCl<sub>2</sub>, BrCl<sub>3</sub>, Br<sub>2</sub>Cl, Br<sub>2</sub>Cl<sub>2</sub>, Br<sub>2</sub>Cl<sub>3</sub>, and Br<sub>3</sub>Cl substituted as well as Br

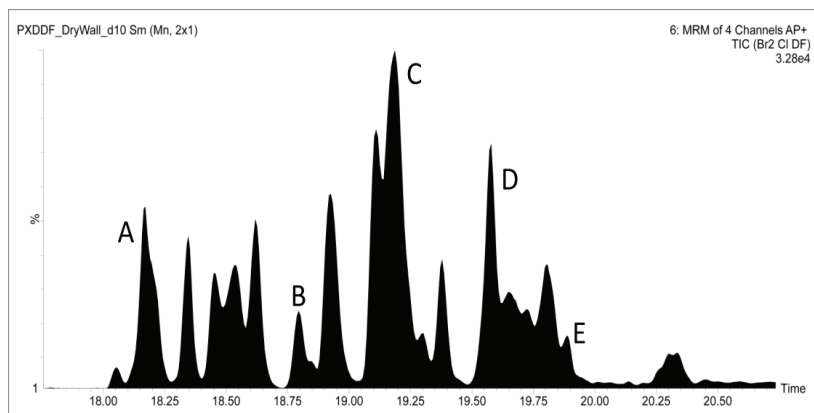


Figure 2. TIC of Br<sub>2</sub>Cl dibenzofuran congener group in an electronics fire sample extract. The following S:N values were calculated for the labeled peaks: A. 46, B. 20, C. 89, D. 62, and E. 12.

Table 2. Range of concentrations (ng/g) of each PXDF identified in the various household and electronics fire debris samples. Results are semi-quantitative due to the complexity of each congener group and the commercial lack of internal standards. Concentrations are reported as the total concentration of all peaks present in the congener group. ND = not detected.

Compound	Household fire	Electronics fire
BrCl DF	0.01–1.42	0.10–21.48
BrCl <sub>2</sub> DF	0.01–0.76	0.26–10.30
BrCl <sub>3</sub> DF	0.01–0.58	0.48–10.05
Br <sub>2</sub> Cl DF	ND–7.63	5.08–88.26
BrCl <sub>4</sub> DF	0.0008–0.07	0.09–5.05
Br <sub>2</sub> Cl <sub>2</sub> DF	ND–5.11	3.53–103.56
Br <sub>2</sub> Cl <sub>3</sub> DF	0.01–0.15	0.86–16.65
Br <sub>3</sub> Cl DF	0.04–5.32	0.48–175.26
Br <sub>3</sub> Cl <sub>2</sub> DF	ND–0.02	0.36–25.84
Br <sub>4</sub> Cl DF	0.02–0.24	2.33–135.50
Br <sub>4</sub> Cl <sub>2</sub> DF	ND–0.003	0.25–43.48
Br <sub>5</sub> Cl DF	ND–0.01	0.77–56.62
Br DF	0.35–40.88	0.33–189.00
Br <sub>2</sub> DF	0.72–82.11	1.68–1468.09
Br <sub>3</sub> DF	0.64–50.40	4.60–6040.79
Br <sub>4</sub> DF	0.77–30.35	6.58–9254.41
Br <sub>5</sub> DF	0.39–7.40	2.88–2725.79
Br <sub>6</sub> DF	0.18–1.45	8.93–1560.32
Br <sub>7</sub> DF	ND	6.93–2349.78

through Br5 substituted.

Peak identifications were made based on retention time ( $R_t$ ) match with a standard, if available. As the number of PXDD/Fs far outweighed the number of available standards, the remaining peaks were identified based on molecular ion isotope patterns, shown in Figure 3.

After the completion of the electronics fire, the firefighters' equipment was coated in black particulate debris. Wipes were taken from the helmets of the firefighters to determine what levels of polyhalogenated dioxins and furans were deposited on the firefighters' equipment. As mentioned previously, these samples turned out to contain the highest levels of PXDFs. These samples represent the fire debris and related particulate matter that first responders are directly exposed to. The tetra-halogenated congeners are typically considered the most toxic, especially when in the 2,3,7,8- substitution pattern. Figure 4 highlights the immense complexity of the helmet samples in each possible tetra-halogenated dibenzofuran group.

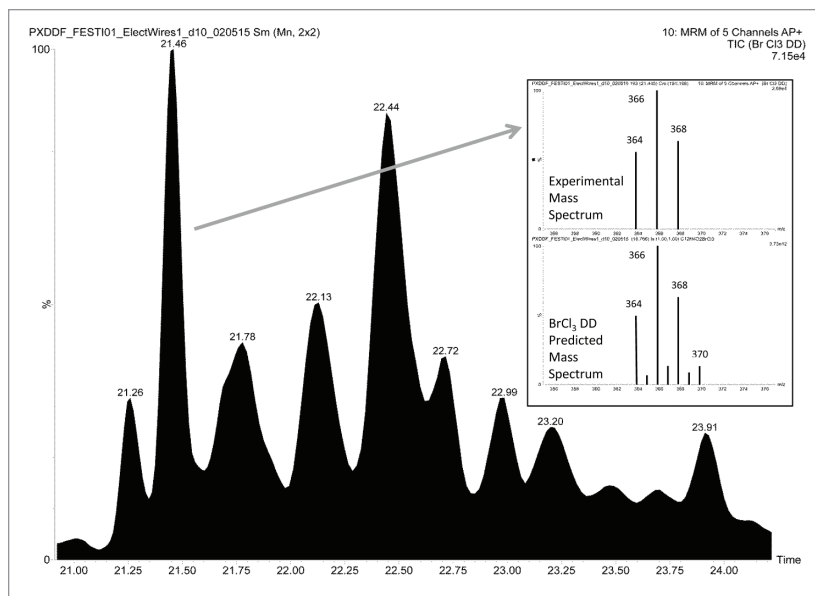


Figure 3. TIC of  $BrCl_3$  dibenzo-*p*-dioxin congener group in an electronics fire sample extract. Inset shows the predicted and experimental isotope pattern match of the molecular ion.

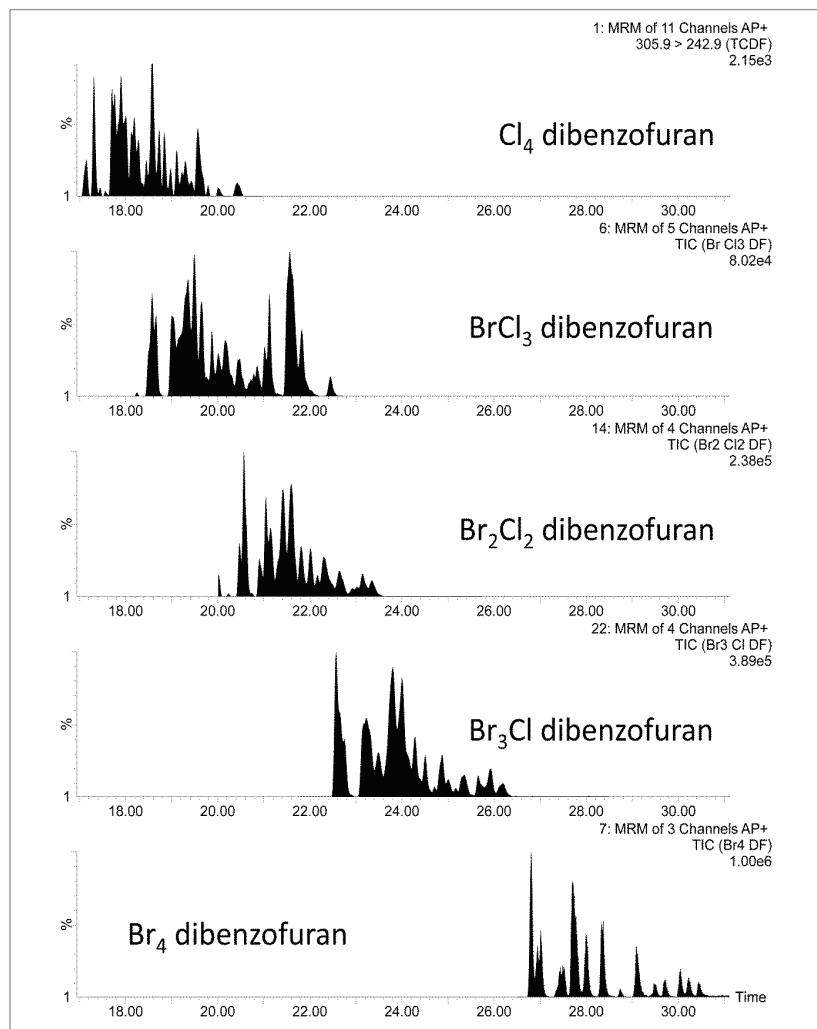


Figure 4. TIC traces of the tetra-halogen substituted dibenzofurans identified on a firefighter helmet.

## CONCLUSIONS

The combination of APGC with the sensitivity of the Xevo TQ-S has allowed for the development of an extensive method for the analysis of polyhalogenated dioxins and furans in a complex sample matrix. Using this method, the analysis of simulated fire debris identified a large range of polybrominated and polyhalogenated dioxins and furans, ranging from mono- through hepta-substituted species. Semi-quantification revealed the total congener concentrations ranged from parts per trillion (ppt) to parts per million (ppm) levels, demonstrating the dynamic range of the analysis with a high level of sensitivity. The types of samples collected and evaluated provide valuable insights into the exposure of firefighters and first responders to these toxic compounds. The particulate samples, such as the samples collected off of the firefighter helmets, contained the highest levels of polyhalogenated dibenzofurans. Demonstrating the complexity of the type of debris first responders are directly exposed to holds implications that the current state of dioxin monitoring does not provide an accurate estimate of the toxicity of such samples. Analysis using APGC-MS/MS brings to light the complex nature of trace level mixed halogenated dioxins and furans present in these fire debris samples.

## Acknowledgements

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## APPENDIX

Appendix Table 1. MRM transitions and appropriate parameters for both PXDD/F and PBDD/F analysis.

Compound name	Start time (min)	End time (min)	Parent (m/z)	Daughter (m/z)	Cone voltage (V)	Collision energy (V)	Fragment	
BrCl DF	12	16.3	279.9	172.9	30	40	-COBr	
			281.9	137.9		50	-COBrCl	
				172.9		40	-COBr	
			295.9	188.9		40	-COBr	
BrCl DD	13.75	18.75	297.9	125.9	30	50	-(CO) <sub>2</sub> BrCl	
				188.9		40	-COBr	
			190.9	40		-COBr		
			313.9	206.9		40	-COBr	
BrCl <sub>2</sub> DF	15.25	19.75	315.9	171.9	30	55	-COBrCl	
				206.9		40	-COBr	
			208.9	40		-COBr		
			315.9	251.9		30	35	<sup>13</sup> C-TCDF
317.9	253.9	35	<sup>13</sup> C-TCDF					
<sup>37</sup> Cl-TCDD	18.5	20.25	327.9	262.9	30	35	<sup>13</sup> CO <sup>37</sup> Cl	
			329.87	264.87		35	<sup>13</sup> CO <sup>37</sup> Cl	
<sup>13</sup> C-TCDD	18.5	20.25	331.9	267.9	30	35	<sup>13</sup> COCl	
			333.9	269.9		35	<sup>13</sup> COCl	
BrCl <sub>2</sub> DD	15.75	19.25	329.9	222.9	30	40	-COBr	
				159.9		50	-(CO) <sub>2</sub> BrCl	
			331.9	161.9		50	-(CO) <sub>2</sub> BrCl	
				222.9		40	-COBr	
BrCl <sub>3</sub> DF	18.2	22.75	347.8	240.8	30	40	-COBr	
				170.8		55	-COBrCl <sub>2</sub>	
			349.8	205.8		50	-COBrCl	
				240.8		40	-COBr	
<sup>13</sup> C-PeCDF	21.25	23.75	349.9	285.9	30	35	<sup>13</sup> COCl	
				287.9		35	<sup>13</sup> COCl	
			365.9	301.9		30	35	<sup>13</sup> COCl
				367.9			303.9	35
Br <sub>2</sub> Cl DF	17.25	20.5	357.8	250.8	30	40	-COBr	
				136.8		55	-COBr <sub>2</sub> Cl	
			359.8	215.8		50	-COBrCl	
				250.8		40	-COBr	
<sup>13</sup> C-BrCl <sub>3</sub> DF	19.75	22.75	359.9	251.9	30	40	<sup>13</sup> COBr	
				253.9		40	<sup>13</sup> COBr	
			363.8	256.8		40	-COBr	
				193.8		50	-(CO) <sub>2</sub> BrCl	
BrCl <sub>3</sub> DD	18.75	24.25	365.8	258.8	30	40	-COBr	
				258.8		40	-COBr	
			367.8	260.8		40	-COBr	
				203.8		50	-(CO) <sub>2</sub> BrCl	
Br <sub>2</sub> Cl DD	17.75	23.75	373.8	266.8	30	40	-COBr	
				266.8		40	-COBr	
			375.8	268.8		40	-COBr	
				274.8		40	-COBr	
BrCl <sub>4</sub> DF	20.75	27.75	381.8	239.8	30	50	-COBrCl	
				276.8		40	-COBr	
			383.8	278.8		40	-COBr	
				385.8		278.8	40	-COBr

Compound name	Start time (min)	End time (min)	Parent (m/z)	Daughter (m/z)	Cone voltage (V)	Collision energy (V)	Fragment
<sup>13</sup> C-HxCDF	25	28.75	385.8	321.8	30	35	<sup>-13</sup> COCl
			387.8	323.8		35	<sup>-13</sup> COCl
<sup>13</sup> C-HxCDD	25	28.75	401.8	337.8	30	35	<sup>-13</sup> COCl
			403.8	339.8		35	<sup>-13</sup> COCl
Br <sub>2</sub> Cl <sub>2</sub> DF	20	25.75	391.8	170.8	30	55	-COBr <sub>2</sub> Cl
				284.8		40	-COBr
			393.8	286.8		40	-COBr
			395.8	288.8		40	-COBr
BrCl <sub>4</sub> DD	23.25	29.75	397.8	290.8	30	40	-COBr
				227.8		50	-(CO) <sub>2</sub> BrCl
			399.8	290.8		40	-COBr
			401.8	292.8		40	-COBr
<sup>13</sup> C-Br <sub>2</sub> Cl <sub>2</sub> DF	22	24.5	405.8	297.8	30	40	<sup>-13</sup> COBr
			407.8	297.8		40	<sup>-13</sup> COBr
Br <sub>2</sub> Cl <sub>2</sub> DD	21.75	26.75	407.8	300.8	30	40	-COBr
				239.8		50	-(CO) <sub>2</sub> BrCl
			409.8	300.8		40	-COBr
			411.8	302.8		40	-COBr
<sup>13</sup> C-HpCDF	29.75	32.75	419.8	355.8	30	35	<sup>-13</sup> COCl
			421.8	357.8		35	<sup>-13</sup> COCl
<sup>13</sup> C-HpCDD	29.75	32.75	435.8	371.8	30	35	<sup>-13</sup> COCl
			437.8	373.8		35	<sup>-13</sup> COCl
<sup>13</sup> C-Br <sub>2</sub> Cl <sub>2</sub> DD	22.75	24.75	421.8	313.8	30	40	<sup>-13</sup> COBr
			423.8	313.8		40	<sup>-13</sup> COBr
Br <sub>2</sub> Cl <sub>3</sub> DF	25	29.75	425.8	318.8	30	40	-COBr
				204.8		55	-COBr <sub>2</sub> Cl
			427.8	320.8		40	-COBr
			429.8	285.8		50	-COBrCl
BrCl <sub>5</sub> DD	28.75	32.25		322.8	30	40	-COBr
			433.8	263.8		50	-(CO) <sub>2</sub> BrCl
				324.8		40	-COBr
			435.8	324.8		40	-COBr
Br <sub>3</sub> Cl DF	21.75	28.5		326.8	30	40	-COBr
			435.8	328.8		40	-COBr
			437.8	330.8		40	-COBr
			439.8	295.8		50	-COBrCl
Br <sub>2</sub> Cl <sub>3</sub> DD	26.75	32.75		330.8	30	40	-COBr
			443.8	326.8		40	-BrCl
			445.8	273.8		50	-(CO) <sub>2</sub> BrCl
				336.8		40	-COBr
Br <sub>3</sub> Cl DD	22.75	27.75	447.8	336.8	30	40	-COBr
				338.8		40	-COBr
			453.7	346.7		40	-COBr
			455.7	283.7		50	-(CO) <sub>2</sub> BrCl
BrCl <sub>6</sub> DD	30.25	35.25		346.7	30	40	-COBr
			457.7	348.7		40	-COBr
			467.7	297.7		50	-(CO) <sub>2</sub> BrCl
				360.7		40	-COBr
Br <sub>3</sub> Cl <sub>2</sub> DF	28.25	32.25	469.7	299.7	30	50	-(CO) <sub>2</sub> BrCl
				362.7		40	-COBr
			469.7	362.7		40	-COBr
			471.7	283.7		45	-COBr <sub>2</sub>
<sup>13</sup> C-OCDD	33.75	35.5		364.7	30	40	-COBr
			473.7	366.7		40	-COBr
			469.7	405.7		35	<sup>-13</sup> COCl
	471.7	407.7	30	35	<sup>-13</sup> COCl		



Compound name	Start time (min)	End time (min)	Parent (m/z)	Daughter (m/z)	Cone voltage (V)	Collision energy (V)	Fragment
Br <sub>3</sub> Cl <sub>2</sub> DD	28	35.75	487.7	317.7	30	50	-(CO) <sub>2</sub> BrCl
				380.7		40	-COBr
				380.7		40	-COBr
			489.7	382.7		40	-COBr
BrCl <sub>7</sub> DD	34.25	37.75	501.7	331.7	30	50	-(CO) <sub>2</sub> BrCl
				394.7		40	-COBr
				333.7		50	-(CO) <sub>2</sub> BrCl
			503.7	396.7		40	-COBr
<sup>13</sup> C-TBDD	29.25	30.75	505.7	398.7	30	40	-COBr
				401.7		40	-COBr
				403.7		40	-COBr
Br <sub>4</sub> Cl DF	30.75	34.25	515.7	408.7	30	40	-COBr
				329.7		50	-COBr <sub>2</sub>
				408.7		40	-COBr
			517.7	412.7		40	-COBr
Br <sub>4</sub> Cl DD	30.5	38	531.7	424.7	30	40	-COBr
				282.8		55	-(CO) <sub>2</sub> Br <sub>2</sub> Cl
				284.8		55	-(CO) <sub>2</sub> Br <sub>2</sub> Cl
				363.8		50	-(CO) <sub>2</sub> BrCl
				424.7		40	-COBr
			535.7	426.7		40	-COBr
Br <sub>4</sub> Cl <sub>2</sub> DF	32.5	36.5	549.6	442.6	30	40	-COBr
				444.6		40	-COBr
				365.6		50	-COBr <sub>2</sub>
			553.6	444.6		40	-COBr
Br <sub>4</sub> Cl <sub>2</sub> DD	31.5	38	565.6	458.6	30	40	-COBr
				397.6		50	-(CO) <sub>2</sub> BrCl
				458.6		40	-COBr
				316.6		55	-(CO) <sub>2</sub> Br <sub>2</sub> Cl
				460.6		40	-COBr
			569.6	462.6		40	-COBr
Br <sub>5</sub> Cl DF	35.75	38.75	595.6	488.6	30	40	-COBr
				409.6		50	-COBr <sub>2</sub>
				490.6		40	-COBr
			599.6	492.6		40	-COBr
Br <sub>5</sub> Cl DD	35	42	611.6	504.6	30	40	-COBr
				360.6		55	-(CO) <sub>2</sub> Br <sub>2</sub> Cl
				441.6		50	-(CO) <sub>2</sub> BrCl
				504.6		40	-COBr
			615.6	502.6		40	-BrCl
Br DF	10	12		506.6	30	40	-COBr
			245.9	138.9		40	-COBr
Br DD	10.5	12.5	247.9	138.9	30	40	-COBr
				154.9		40	-COBr
			261.9	126.9		50	-(CO) <sub>2</sub> Br <sub>2</sub>
Br <sub>2</sub> DF	14	17	263.9	154.9	30	40	-COBr
				216.9		40	-COBr
Br <sub>2</sub> DD	14	20	323.9	216.9	30	50	-COBr <sub>2</sub>
				137.9		40	-COBr
			325.9	218.9		40	-COBr
Br <sub>3</sub> DF	19	23	339.9	232.9	30	40	-COBr
				206.9		50	-(CO) <sub>2</sub> Br <sub>2</sub>
			341.9	234.9		40	-COBr
Br <sub>3</sub> DD	20	27		215.8	30	50	-COBr <sub>2</sub>
				296.8		40	-COBr
			403.8	298.8		40	-COBr
Br <sub>3</sub> DD	20	27	405.8	298.8	30	40	-COBr
				312.8		40	-COBr
				286.8		50	-(CO) <sub>2</sub> Br <sub>2</sub>
			419.8	314.8		40	-COBr

Compound name	Start time (min)	End time (min)	Parent (m/z)	Daughter (m/z)	Cone voltage (V)	Collision energy (V)	Fragment
Br <sub>4</sub> DF	26.5	32.5	481.7	374.7	30	40	-COBr
			483.7	295.7		50	-COBr <sub>2</sub>
				376.7		40	-COBr
Br <sub>4</sub> DD	26.5	33	497.7	390.7	30	40	-COBr
			499.7	364.7		50	-(CO) <sub>2</sub> Br <sub>2</sub>
				392.7		40	-COBr
Br <sub>5</sub> DF	30.5	38.5	561.6	373.6	30	50	-COBr <sub>2</sub>
				454.6		40	-COBr
			563.6	456.6		40	-COBr
Br <sub>5</sub> DD	31	39	577.6	442.6	30	50	-(CO) <sub>2</sub> Br <sub>2</sub>
				470.6		40	-COBr
			579.6	472.6		40	-COBr
Br <sub>6</sub> DF	35	44.5	639.5	532.5	30	40	-COBr
			641.5	453.5		50	-COBr <sub>2</sub>
				534.5		40	-COBr
Br <sub>6</sub> DD	35	44.5	655.5	548.5	30	40	-COBr
				522.5		50	-(CO) <sub>2</sub> Br <sub>2</sub>
			657.5	550.5		40	-COBr
Br <sub>7</sub> DF	43	61	719.4	531.4	30	50	-COBr <sub>2</sub>
				612.4		40	-COBr
			721.4	614.4		40	-COBr
Br <sub>7</sub> DD	43	61	735.4	600.4	30	50	-(CO) <sub>2</sub> Br <sub>2</sub>
				628.4		40	-COBr
			737.4	630.4		40	-COBr
Br <sub>8</sub> DF	48	61.56	797.3	690.3	30	40	-COBr
			799.3	611.3		50	-COBr <sub>2</sub>
				692.3		40	-COBr
Br <sub>8</sub> DD	50	61.56	813.3	706.3	30	40	-COBr
			815.3	680.3		50	-(CO) <sub>2</sub> Br <sub>2</sub>
				708.3		40	-COBr