

# Analysis of Combustion Byproducts on Firefighter Protection Equipment Using a Novel High-Resolution GC/Q-TOF

## Application Brief

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### Introduction

Cancer is a leading cause of fire service morbidity and mortality [1,2]. During a fire, firefighters are exposed to smoke and elevated levels of organic chemicals, such as flame retardants, originating from furniture, carpets, and so forth, as well as their combustion by-products. A high-resolution MS used in full spectrum acquisition mode is extremely advantageous for the untargeted analysis of the environmental contaminants in complex matrices, especially for identification of trace compounds. To identify polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs) and other combustion products, we used a novel high-resolution Agilent 7250 GC/Q-TOF.



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## Experimental

### Sample collection and extraction method

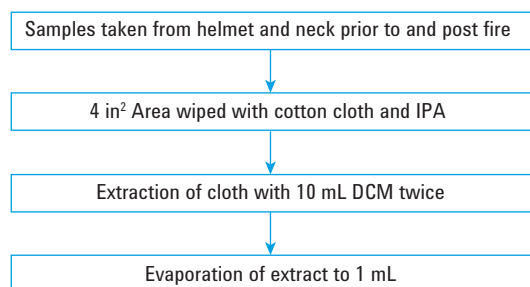


Figure 2. Sample collection and extraction workflow.

### Analysis

GC/MS analysis was performed using an Agilent 7890B GC system coupled to a novel high-resolution (25,000 at  $m/z$  272) Agilent 7250 GC/Q-TOF, equipped with a low-energy capable EI source.

Table 1 shows the instrument parameters.

Table 1. Instrument Parameters for Agilent 7250 GC/Q-TOF Analysis

Parameter	Value
Column	Agilent DB-5MS, 0.25 mm × 30 m, 0.25 μm
Injection volume	1 μL
Injection mode	Splitless
Split/Splitless inlet temperature	280 °C
Oven temperature program	50 °C for 3 minutes, 10 °C/min to 300 °C, 7 minutes hold
Carrier gas	Helium at 1.5 mL/min, constant flow
Transfer line temperature	300 °C
Ionization mode	Standard EI at 70 eV Low energy EI at 15 eV and 12 eV
Source temperature, 70 eV/15 eV or less	240 °C/200 °C
Quadrupole temperature	150 °C
Mass range	50 to 1,200 $m/z$
Spectral acquisition rate	5 Hz

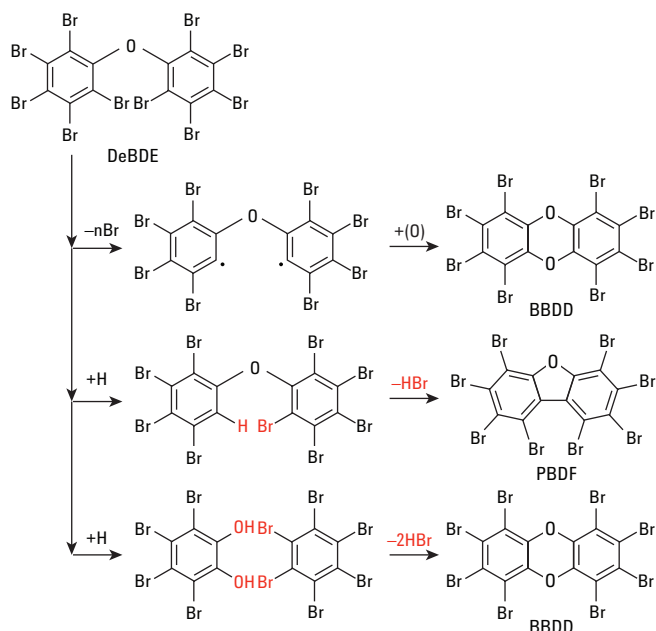


Figure 1. Decomposition of PBDEs, and formation of dioxin and furan structures.

## Data analysis

The data were acquired using a 7250 accurate mass high-resolution GC/Q-TOF system. First, the data were processed using the feature detecting algorithm SureMass in Unknowns Analysis B.08.00. Initial compound identification was performed by spectrum comparison with NIST14 El library and confirmed by retention index (RI) matching when possible (Figure 3). Based on Unknowns Analysis

results, a Quant method was created in Agilent MassHunter Quantitative Analysis software B.08.00 for semiquantification of PAHs as well as PAH-like compounds (Figure 4). PBDEs and molecular ions of unknown brominated compounds were identified with the help of low electron energy compound spectra. Molecular ions were confirmed by evaluating the entire isotopic cluster for  $m/z$ , relative isotope abundance, and isotope ratios using Molecular Formula Generator (MFG) of MassHunter Qualitative Analysis B.08.00.

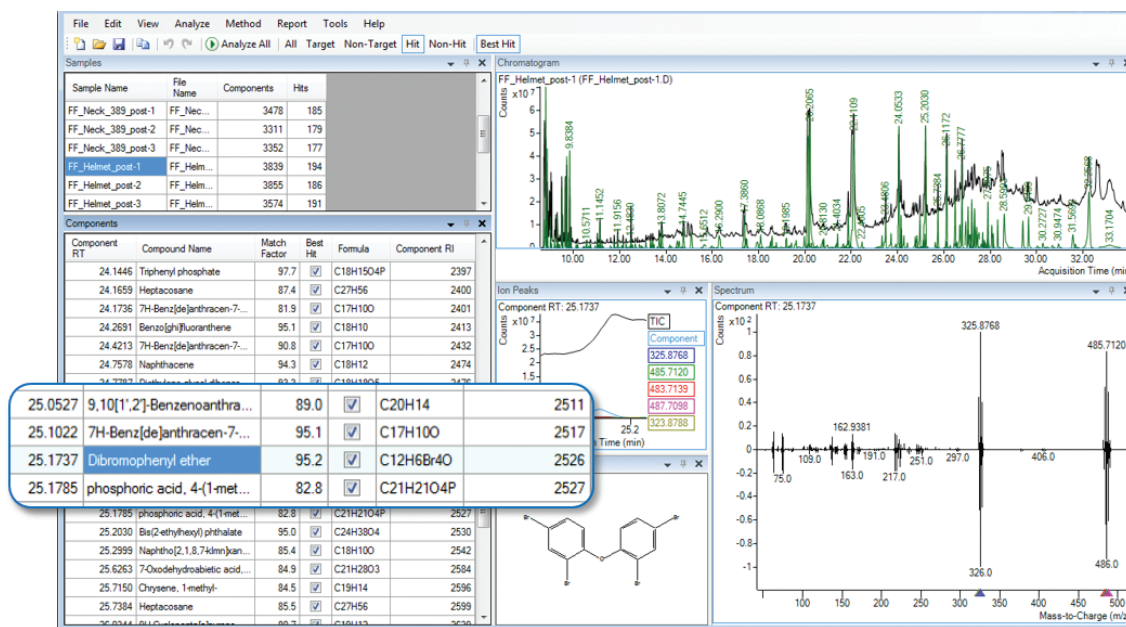


Figure 3. Unknowns Analysis B.08.00 and spectrum comparison with NIST14.

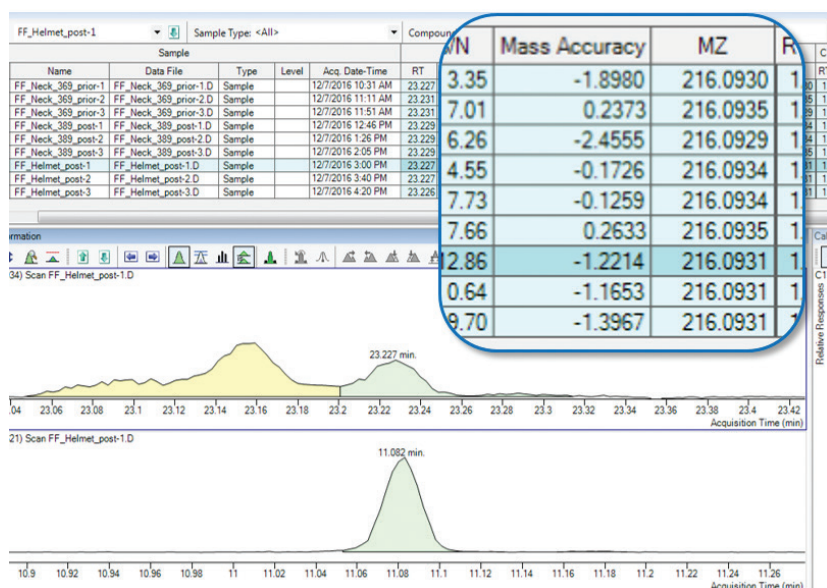


Figure 4. Quantitation of PAHs using Agilent MassHunter Quant B.08

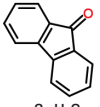
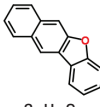
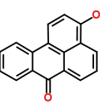
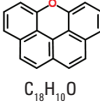



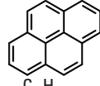

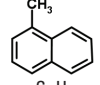



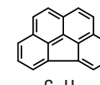
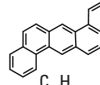
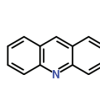
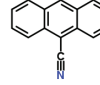
## Results and Discussion

### PAH Identification

PAHs were identified in all post fire samples. Over 50 PAH species were identified on the helmet post fire. Regulated PAHs that were identified using NIST14 were confirmed by retention index. Table 2 summarizes examples of identified PAHs and PAH-like compounds on the helmet post fire.

Potential structures of the identified formulas are suggested in Table 2. These are similar to the PAHs that were detected by Fernando, *et al.* [3] in the air and on the skin of firefighters post fire.

Table 2. Combined List of Identified PAHs **Note:** For Most of the PAH and PAH-like Formulas, Multiple Isomers were Identified

Compound/formula	m/z	Avg mass error (ppm)	Compound/formula	m/z	Avg mass error (ppm)	Compound/formula	m/z	Avg mass error (ppm)
<b>Regulated PAHs</b>			<b>Other PAHs</b>			<b>O-containing PAHs</b>		
Naphthalene [C <sub>10</sub> H <sub>8</sub> ]	128.0626	1.01	C <sub>10</sub> H <sub>12</sub>	132.0934	0.91	C <sub>13</sub> H <sub>8</sub> O	180.057	0.90
Acenaphthylene [C <sub>12</sub> H <sub>8</sub> ]	152.0626	0.82	C <sub>11</sub> H <sub>14</sub>	146.109	1.07	C <sub>16</sub> H <sub>10</sub> O	218.0726	1.47
Acenaphthene [C <sub>12</sub> H <sub>10</sub> ]	154.07825	0.35	C <sub>11</sub> H <sub>10</sub>	142.0777	0.55	C <sub>17</sub> H <sub>10</sub> O	230.0726	1.99
Fluorene [C <sub>13</sub> H <sub>10</sub> ]	166.07825	1.15	C <sub>12</sub> H <sub>16</sub>	160.1247	1.22	C <sub>17</sub> H <sub>10</sub> O <sub>2</sub>	246.0675	1.27
Phenanthrene [C <sub>14</sub> H <sub>10</sub> ]	178.07825	1.25	C <sub>12</sub> H <sub>12</sub>	156.0934	1.07	C <sub>18</sub> H <sub>10</sub> O	242.0726	2.03
Anthracene [C <sub>14</sub> H <sub>10</sub> ]	178.07825	0.96	C <sub>13</sub> H <sub>12</sub>	168.0934	1.14	C <sub>18</sub> H <sub>10</sub> O <sub>2</sub>	258.0675	1.15
Fluoranthene [C <sub>16</sub> H <sub>10</sub> ]	202.07825	1.06	C <sub>14</sub> H <sub>14</sub>	182.109	0.59	C <sub>20</sub> H <sub>12</sub> O	268.0883	1.68
Pyrene [C <sub>16</sub> H <sub>10</sub> ]	202.07825	1.51	C <sub>15</sub> H <sub>12</sub>	192.0934	0.53			
Benz[a]anthracene [C <sub>18</sub> H <sub>12</sub> ]	228.0939	1.27	C <sub>15</sub> H <sub>10</sub>	190.0777	2.57			
Chrysene [C <sub>18</sub> H <sub>12</sub> ]	228.0939	1.07	C <sub>18</sub> H <sub>22</sub>	238.1716	1.07			
Benzo[b]fluoranthene [C <sub>20</sub> H <sub>12</sub> ]	252.0939	1.81	C <sub>18</sub> H <sub>18</sub>	234.1403	1.04			
Benzo[k]fluoranthene [C <sub>20</sub> H <sub>12</sub> ]	252.0939	2.23	C <sub>17</sub> H <sub>12</sub>	216.0934	0.87			
Benzo[a]pyrene [C <sub>20</sub> H <sub>12</sub> ]	252.0939	1.79	C <sub>18</sub> H <sub>10</sub>	226.0777	0.92			
Indeno[1,2,3-cd]pyrene [C <sub>22</sub> H <sub>12</sub> ]	276.0939	1.65	C <sub>20</sub> H <sub>14</sub>	254.109	1.05			
Dibenz[a,h]anthracene [C <sub>22</sub> H <sub>14</sub> ]	278.10955	1.55	C <sub>19</sub> H <sub>14</sub>	242.109	0.58			
Benzo[ghi]perylene [C <sub>22</sub> H <sub>12</sub> ]	276.0939	1.73	C <sub>19</sub> H <sub>12</sub>	240.0934	2.17			
	C <sub>10</sub> H <sub>8</sub>		C <sub>22</sub> H <sub>14</sub>	278.10955	0.91	<b>Compound/formula</b>	<b>m/z</b>	<b>Avg mass error (ppm)</b>
	C <sub>12</sub> H <sub>8</sub>		C <sub>24</sub> H <sub>18</sub>	306.1403	1.67	<b>N-containing PAHs</b>		
	C <sub>14</sub> H <sub>10</sub>		C <sub>22</sub> H <sub>12</sub>	276.0939	2.25	C <sub>13</sub> H <sub>9</sub> N	179.073	1.24
	C <sub>16</sub> H <sub>10</sub>					C <sub>12</sub> H <sub>9</sub> N	167.073	1.55
	C <sub>18</sub> H <sub>12</sub>			C <sub>11</sub> H <sub>10</sub>		C <sub>15</sub> H <sub>9</sub> N	203.073	1.52
	C <sub>20</sub> H <sub>12</sub>			C <sub>12</sub> H <sub>12</sub>		C <sub>17</sub> H <sub>11</sub> N	229.0886	0.63
	C <sub>22</sub> H <sub>12</sub>			C <sub>18</sub> H <sub>10</sub>		C <sub>19</sub> H <sub>11</sub> N	253.0886	1.08
	C <sub>22</sub> H <sub>14</sub>						C <sub>13</sub> H <sub>9</sub> N	
							C <sub>15</sub> H <sub>9</sub> N	

Based on relative abundances, fluoranthene, pyrene, and the larger PAHs were the predominant PAHs measured on the helmet post fire. Figure 5 illustrates the abundances of PAHs and PAH-like compounds on the helmet post fire.

Figure 6 shows the sum of PAHs, O-containing PAHs, and N-containing PAHs in all samples. The PAHs on the helmet post fire exceeded the concentration on the skin. The post fire skin samples exhibited greater concentrations of all groups of PAHs.

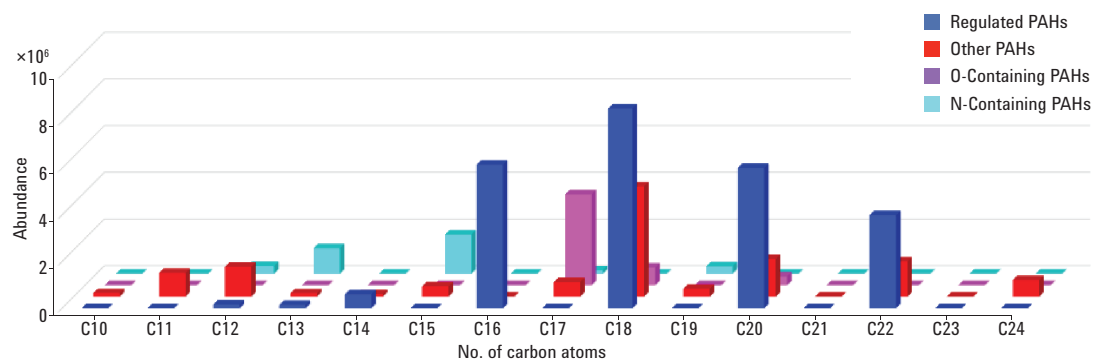


Figure 5. PAHs and PAH-like compounds on post fire wipe of helmet.

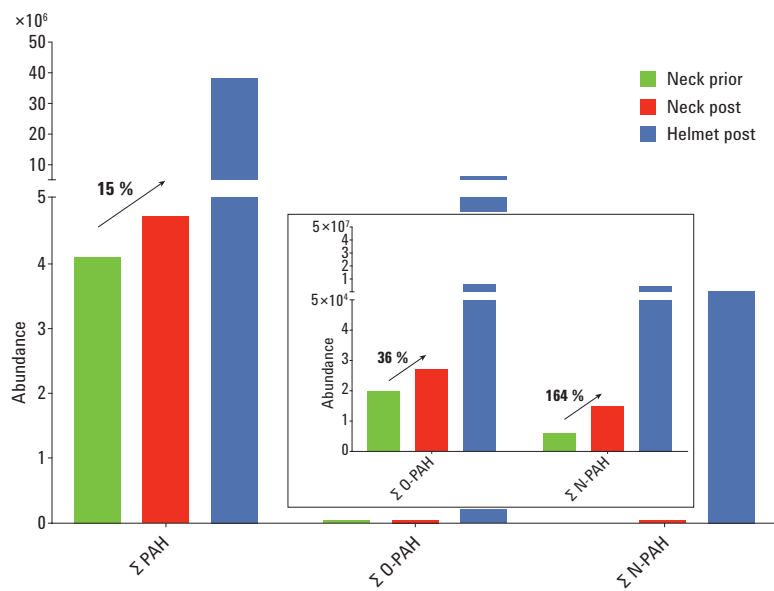


Figure 6. Total PAHs identified in pre and post fire wipes.

## Brominated compounds

Brominated compounds were detected only in post fire samples, indicating that they originated from exposure to smoke.

Isomers of tri-BDE, tetra-BDE, penta-BDE, and hexa-BDE originating from burned material containing flame retardants were detected on the neck and helmet post fire. Table 3 summarizes the relative abundances. The retention times were verified using native standards.

Other Br-containing compounds were found only on the helmet post fire, but not on the neck. These are potential PBDE combustion byproducts (for example,  $C_6H_4Br_2O$ ) and brominated PAHs (for example,  $C_{16}H_9Br$ ). Figures 7 and 8 illustrate the mass spectra of a few brominated compounds at different electron energies. Low electron energies facilitated the identification of molecular ions of the unknown compounds.

Table 3. List of Identified PBDE and Other Brominated Compounds Identified in Post Fire Samples

Formula	<i>m/z</i>	Mass error (ppm)*	Resolving power	MFG score	Verified by standard	Retention time (min)	Neck: Prefire, % abundance	Neck: Post fire, % abundance	Helmet: Post fire, % abundance
$C_6H_4Br_2O$	249.8623	1.7	27336	98.34		13.15	n.d.	n.d.	15.26
$C_{14}H_{21}BrO$	284.077	0.92	26911	90.92		16.409	n.d.	n.d.	31.17
$C_7H_8Br_2N_2$	277.9049	0.22	27495	88.15		19.891	n.d.	n.d.	5.72
$C_7H_6Br_2N_2O$	291.8841	0.99	26072	90.08		20.832	n.d.	n.d.	13.84
$C_{10}H_9BrN_2$	235.9944	1.27	27136	97.41		21.122	n.d.	n.d.	1.53
$C_{16}H_9Br$	279.9882	1.69	26187	98.71		24.609	n.d.	n.d.	4.39
$C_{15}H_{14}Br_2O_2$	383.9355	0.25	29880	95.36		25.88	n.d.	n.d.	0.32
$C_{12}H_7Br_3O$	403.8047	0.45	31609	90.67	Tri-BDE	22.687	n.d.	1.1	0.29
		0.23	29157	96.13		23.063	n.d.	1.41	0.4
$C_{12}H_6Br_4O$	481.7152	1.36	30425	91.87	Tetra-BDE	24.835	n.d.	0.9	0.4
		2.62	31364	95.40		25.175	n.d.	58.84	13.09
		1.15	27322	93.01		25.507	n.d.	0.69	0.3
$C_{12}H_5Br_5O$	559.6257	2.59	30367	95.05	Penta-BDE	26.684	n.d.	8.99	2.74
		2.03	30813	94.57		27.159	n.d.	25.29	9.26
		1.24	29448	91.29		27.974	n.d.	1.1	0.35
$C_{12}H_4Br_6O$	637.5357	0.7	30817	91.38	Hexa-BDE	28.335	n.d.	0.83	0.51
		1.7	31299	94.73		29.058	n.d.	0.85	0.43

\* Mass error is calculated as a weighted average mass error for the entire isotopic cluster.

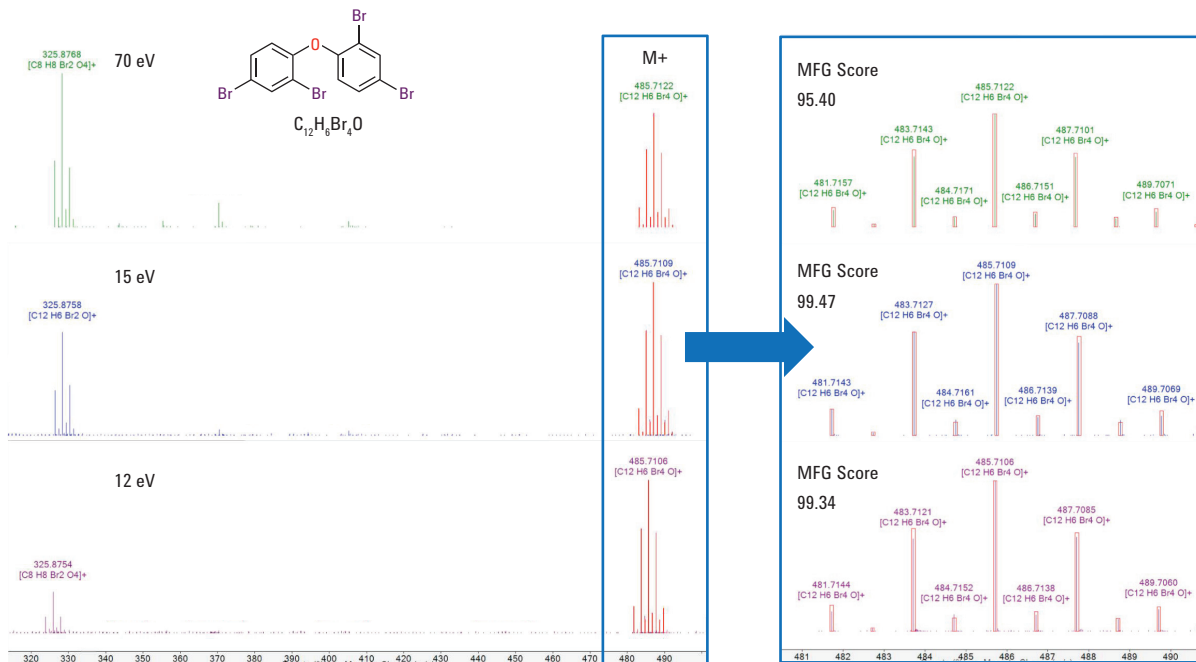


Figure 7. Example of PBDE detected on neck wipe post fire. MFG score is based on mass accuracy, isotope spacing as well as relative isotope abundance ratios.

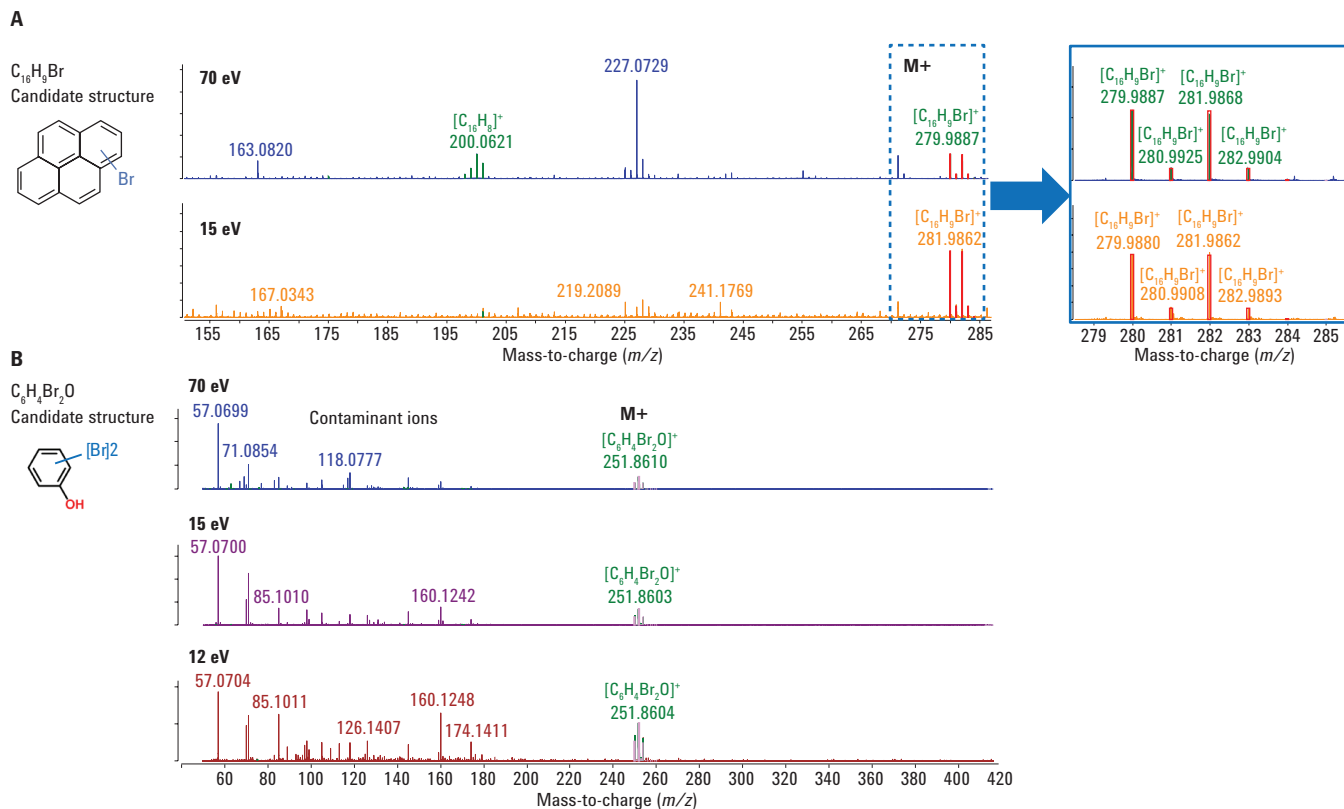


Figure 8. Examples of the unknown brominated compounds spectra at different electron energies. Spectra are annotated using MFG tool with Fragment Formula Annotation. Unannotated ions are likely contaminant ions originated from coeluting compounds. Candidate structures based on 70 eV and low electron energy spectra are shown on the left.

## Conclusions

Neck wipes collected post fire showed that the hood did not fully protect from smoke-related contaminants. PAHs as well as PBDEs and other brominated compounds were found on the neck and helmet of firefighters post fire. Due to their low detection limits, brominated compounds can act as biomarkers of exposure of firefighters to smoke.

The applied GC/Q-TOF method proved to be very sensitive and selective in detecting numerous PAHs, PBDEs, and other brominated combustion byproducts.

A low-energy-capable EI source facilitated identification of the molecular ions of the unknown brominated compounds.

## References

1. M. N. Bates. "Registry-based case-control study of cancer in California firefighters" *Am. J. Ind. Med.* **50** (5), 339-344 (2007).
2. D. Kang, *et al.* "Cancer incidence among male Massachusetts firefighters 1987-2003" *Am. J. Ind. Med.* **51**(5), 329-335 (2008).
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