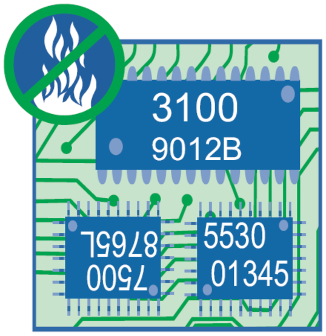
United States
Environmental Protection
Agency

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS



APPENDICES

August 2015

FINAL REPORT

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX A

Yamada, Takahiro; Striebich, Richard. Open-burning, Smelting, Incineration, Off-gassing of Printed Circuit Board Materials Phase I Flow Reactor Experimental Results Final Report. Environmental Engineering Group, UDRI. August 11, 2008

Open-burning, Smelting, incineration, off-gassing of printed circuit board materials, Phase I Flow Reactor Experimental Results
Final Report (August 11, 2008)

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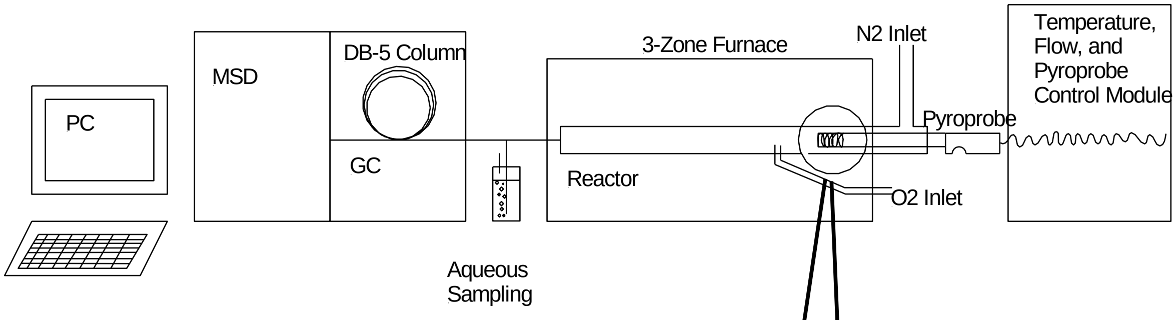
1. Introduction and Background

In this study we investigated the controlled exposure of various printed circuit boards (PCBs) laminates to high temperature conditions. This work, combined with more realistic combustion studies (Cone Calorimeter) will allow us to better understand the mechanisms of PCB thermal destruction. This information will be used to evaluate existing and candidate flame retardants used in the manufacturing of the PCBs. The combination of better controlled experiments with actual combustion experiments will allow researchers and manufacturers to determine whether candidate flame retardant material is better or worse than the existing formulations.

2. Experimental Setup

Figures 1 and 2 show an overview photo and a schematic of the experimental setup designed for the project. A straight 28.5” long quartz reactor with 9.5×7mm o.d.×i.d. (QSI, Fairport Harbor, OH) was used for pyrolysis experiments, and same reactor with 3×1mm i.d.×o.d. stem attached to the straight main reactor at 5 ¼” from the reactor inlet end (QSI, Fairport Harbor, OH, custom order) was used for the oxidation experiments. The narrow tubing was installed to introduce oxygen for the combustion tests. Figure 3 shows detailed design of the modified reactor. New reactor was used for each sample for pyrolysis experiments (100% N_2). The same reactor was used for the experiment with 10 and 21% O_2 and N_2 as bath gas. The samples were gasified under pyrolytic condition for all experiments as seen in Figure 2. Blank experiments were performed for each experiment, both pyrolysis and oxidation, to ensure that there was no carry over from the previous experiments. The reactors were installed into 3-zone temperature controlled furnace, ¾” diameter and 24” length, SST-0.75-0-24-3C-D2155-AG S-LINE (Thermocraft, Winston-Salem, NC.).

Figure 1. Overview of experimental Setup



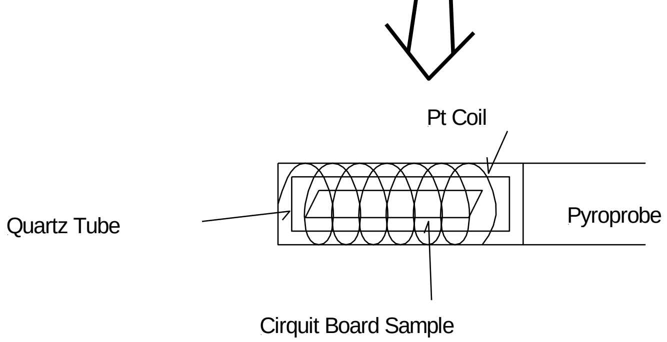


Figure 2. Schematic of experimental setup used for this project

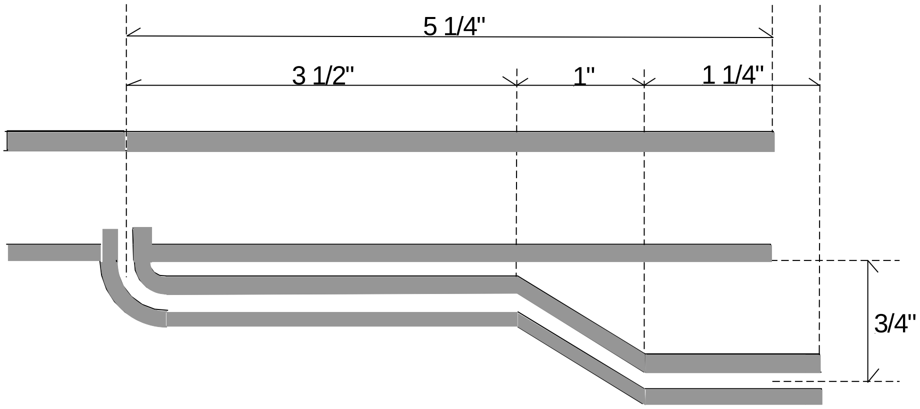


Figure 3. Detailed schematic of reactor inlet

Figure 4 shows the reactor temperature profiles at 300, 700, and 900ºC. Based on the profiles, effective length was determined to be 18” (from 6” to 24”). The effective length was used to set gas flow rate to maintain 2 sec. of residence time for each temperature. The transfer line between the reactor and GC oven was heated above 250ºC.

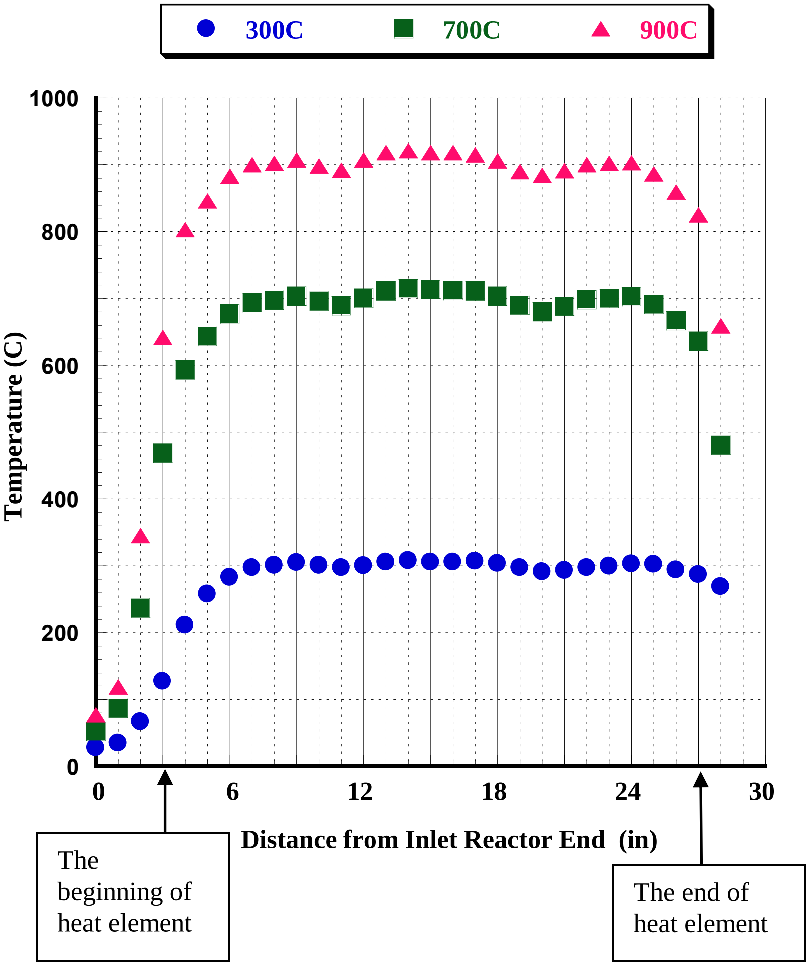


Figure 4. Reactor temperature profiles for 300, 700, and 900°C

As shown in Figure 5, samples were gasified using a pyroprobe, CDS 120 Pyroprobe (CDS analytical Inc., Oxford, PA). The sample (circuit board laminate) was cut into a small piece, 1.5 - 2 mm wide × 1cm long, and inserted into quartz cartridge, 3×4mm i.d.×o.d. 1" length (CDS analytical Inc. Oxford, PA) as shown in Figure 6. The cartridge was then inserted into pyroprobe for the gasification. When the sample was gasified, the pyroprobe temperature was increased from room temperature to 900°C with a 20°C/ms ramp rate and held for 20 sec. at the final temperature. The gasification process was repeated 3 times to ensure complete gasification. The exhaust gas was passed through an impinger containing 20mL HPLC grade ultra-pure water (Alfa Aesar, Ward Hill, MA) in a 40mL amber vial (WHEATON Industries Inc., Millville, NJ). A small part of gas (1mL/min. flow rate) was introduced to Gas chromatograph / Mass Spectrometer (HP 5890/5970 GC/MSD, Hewlett Packard, Pasadena, CA). The GC column used for the analyte separation was DB-5MS, 30m length, 0.25mm i.d., 0.25µm thickness (Agilent J&W, Foster City, CA).


Figure 5. Pyroprobe Pt filament

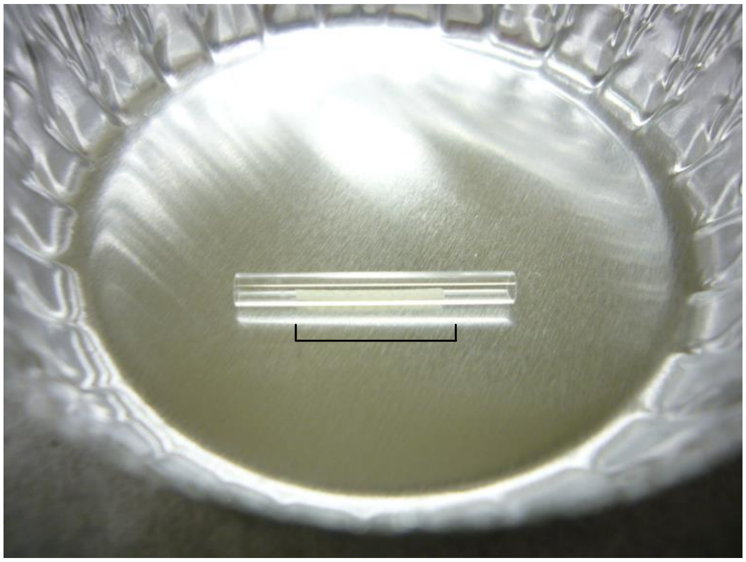


Figure 6. Pyroprobe cartridge with sample

3. Experimental Conditions

Table 1 and 2 show the experimental conditions that were investigated in Phase I of the flow reactor study. For the sample without copper laminate both pyrolysis and oxidation experiments were performed. The samples with copper laminate were only subject to pyrolysis. Selected experiments were repeated for pyrolysis at 700ºC and 21% O_2 at 900ºC. The oxygen concentrations of 10 and 21% were obtained by mixing nitrogen with 50% oxygen. The tables describe experiments conducted on a "no Flame Retardant" sample (NFR), a conventional "Brominated Flame Retardant" sample (BrFR), and candidate phosphorus sample (PFR).

Table 1 Experimental condition for the samples without Cu laminate (Unit: ºC)

Sample	N_2	10% O_2	21% O_2
NFR	300, 700, 900	700	700, 900
BrFR	300, 700	700	300, 700, 900
PFR	300, 700	700	300, 700, 900

Table 2 Experimental condition for the samples with Cu laminate (Smelting) (Unit: ºC).

Sample	N_2
NFR w/Cu	900
BrFR w/Cu	900
PFR w/Cu	900

Table 3 shows N_2 and O_2 (50%) flow rates for each temperature and oxygen concentration. The flow rate was set to obtain 2 sec. residence time in the flow reactor, 18" length × 7mm i.d.

Table 3 N2, O2, and total flow rate used for each experimental condition (Unit: mL/min).

Temperature	O_2 Conc. (%)	N_2	O_2 (50%)	Total
300	0	274	0	274
	21	159	115	274
700	0	162	0	162
	10	130	32	162
	21	94	68	162
900	0	134	0	134
	21	78	56	134

4. Results

4.1 TGA

Prior to the flow reactor incineration tests, thermogravimetric analysis (TGA) was conducted to determine final gasification temperatures. TGA for all samples in N2 and air environments are shown in Tables A1 to A6 of Appendix A. Table 4 shows initial and final gasification temperatures for each sample in N_2 and air environments. The gasification initial and final gasification temperatures vary for each sample. Those temperatures were lower when air was used for the gasification in general. No weight loss was observed over 900ºC for all samples; therefore, pyroprobe final gasification temperature was set to 900ºC.

Table 4 Sample gasification starting and final temperatures, and its weight loss

Sample	Gasification Environment	Approx. Starting Temperature (ºC)	Approx. Final Temperature (ºC)	Weight Loss (%)
Non-flame Retardant w/Cu	N_2	350	900	15.0
Non-flame Retardant	N_2	350	900	31.5
Non-flame Retardant	Air	300	650	45.9
Bromine Flame Retardant w/Cu	N_2	300	800	22.5
Bromine Flame Retardant	N_2	300	900	39.4
Bromine Flame Retardant	Air	250	650	48.4
Phosphorous Flame Retardant w/Cu	N_2	350	900	18.6
Phosphorous Flame Retardant	N_2	350	900	32.0
Phosphorous Flame Retardant	Air	350	750	47.3

4.2 Major Combustion Byproduct Analysis

The major peaks of the total ion chromatograms (TIC) were identified for the each flame retardant sample and experimental condition. Samples were introduced into the GC oven at a flow rate of 1mL/min., and cryogenically trapped at -30ºC during combustion tests. After the sample gasification and combustion, helium was introduced into the system for 3 minutes to sweep the reactor system and pressurize GC column. The oven was, then, heated at 20ºC/min ramp rate up to 300ºC and held 10 minutes. The results are shown in Figure B1 to B27 in Appendix B. Some of the experiments were repeated to examine the consistency of the experimental device. The repeatability experiments were conducted for the pyrolysis at 700ºC, and combustion with 21% O_2 at 900ºC for each of three samples. The results from these experiments are shown in Figure 3B, 8B, 12B, 17B, 22B, and 27B in Appendix B. Most of the compounds identified were aromatics. The most prevalent compounds from most pyrolysis and oxidation experiments were benzene, toluene, xylene and its isomers, phenol, methylphenol and its isomers, dimethyl phenol and its isomers, styrene, benzofuran and its derivatives, dibenzofuran and its derivatives, xanthene, naphthofuran and its derivative, naphthalene, biphenyl, biphenylene, fluorine, phenanthrene/anthracene. Major brominated compounds found from the brominated flame retardant include bromo - and dibromo-phenols and hydrogen bromide. Five largest peaks for each sample are listed in Table 5 for each temperature and oxygen concentration. Phenol, methylphenol, toluene, xylene, and benzene were often observed as major products. Dibromophenol was observed for brominated flame retardant at low temperature, and HBr was major brominated compound at the high temperature. Combined with TIC shown in Appendix B, it is observed that in the pyrolytic environment (100%N_2) brominated flame retardant reduces number of byproducts at all temperatures, especially effective at low temperature (300ºC). In the oxidative environment (10 and 21% O_2) the brominated flame retardant also reduces both number of combustion byproducts and their amount at all temperatures. Phosphorous flame retardant reduces amount of combustion byproducts. Increased oxygen level reduces number and amount of combustion byproducts. Increased temperature also reduces number and amount of combustion byproducts, and byproducts are decomposed to smaller compounds at the high temperature. Number of brominated compounds were found at the trace level, and the identification of these compounds is described in Section 4.3. No phosphorous containing combustion byproducts were identified from the major peak of phosphorous flame retardant combustion test. Phosphorus flame retardant combustion tests at 900C with 21% oxygen were repeated after the completion of a series of combustion tests which produced skeptical results. When experiments were conducted under this condition initially, only water was observed with very minor combustion byproduct peaks. When experiments were repeated later, combustion byproducts were observed. TICs shown in Figure B26 and 27 are results from the repeated experiments. The reason why only water was observed is still unknown; however, problems with the mass selective detector (MSD) at that time could have caused poor sensitivity. Byproducts observed in these most recent experiments were more consistent with similar conditions and reactant feeds. Table 6 summarizes amount of sample gasified and its weight loss.

Table 5. Major Combustion Byproducts under Different Experimental Conditions

Temp. (ºC)	Environment	Major Combustion Byproducts (5 largest peaks in this order, top to bottom) and Remarks		
		Non-FR	Br-FR	P-FR
300	Pyrolysis	Phenol Methylphenol Toluene Xylene Xanthene	Phenol Methylethylphenol Methylphenol Dibromophenol Toluene (only mono-ring aromatics as a major peaks)	Phenol Methylphenol Dimethylpehnol Toluene Benzene
	Oxidation (21%)	N.A.	Benzene Methylethylphenol Bromophenol Dibromophenol Tetramethylbenzene	Phenol Methylphenol Dimethylphenol Toluene Xylene
700	Pyrolysis	Phenol Methylphenol Toluene Xylene Benzene	Phenol Toluene Benzene Methylphenol Methylbenzofuran (HBr observed)	Phenol Methylphenol Toluene Benzene Xylene

Table 5. Major Combustion Byproducts under Different Experimental Conditions (Cont'd)

Temp. (ºC)	Environment	Major Combustion Byproducts (5 largest peaks with this order, top to bottom) and Remarks		
		Non-FR	Br-FR	P-FR
700	Oxidation (10%)	Phenol Benzene Toluene Methylphenol Styrene	Benzene Phenol Toluene Styrene Naphthalene (next biggest is bromophenol, then HBr)	Phenol Benzene Toluene Methylphenol Styrene
700	Oxidation (21%)	Benzene Phenol Benzofuran Toluene Styrene	Phenol Benzene HBr Dibenzofuran Naphthalene	Benzene Phenol Toluene Styrene Methylbenzofuran
900	Pyrolysis	Benzene Toluene Naphthalene Biphenylene Benzofuran	Benzene Toluene Naphthalene Styrene Indene	Benzene Naphthalene Toluene Biphenylene Anthracene
	Oxidation (21%)	Benzene Naphthalene Benzofuran Toluene Biphenylene (Benzene and naphthalene are the major products, others are minor)	Benzene Naphthalene HBr Phenanthrene Benzonitrile	Benzene Naphthalene Phenanthrene Toluene Biphenylene

Table 6. Amount of Samples Gasified and Their Gasification Rates

Sample	O_2 Conc. (%)	Temp. (C)	Sample Loaded (g)	Amount Gasified (g)	Gasification % by weight	Remarks
NFR	0	300	0.013644	0.005086	37.3	
		700	0.013336	0.005013	37.6	
			0.014391	0.005431	37.7	Duplicate
		900	0.013610	0.005175	38.0	
	10	700	0.012586	0.004722	37.5	
	21	700	0.013780	0.005072	36.8	
		900	0.013405	0.004966	37.0	
			0.012944	0.004566	35.3	Duplicate
NFR w/Cu	0	900	0.022023	0.004382	19.9	

Table 6. Amount of Sample Gasified and its Gasification Rate (Cont'd)

Sample	O_2 Conc. (%)	Temp. (C)	Sample Loaded (g)	Amount Gasified (g)	Gasification % by weight	Remarks
BrFR	0	300	0.012237	0.004501	36.8	
		700	0.013009	0.005157	39.6	
			0.012614	0.004855	38.5	Duplicate
	10	700	0.014123	0.005989	42.4	
	21	300	0.010710	0.003761	35.1	
		700	0.012087	0.004404	36.4	
		900	0.012065	0.004564	37.8	
			0.011910	0.004450	37.3	Duplicate
BrFR w/Cu	0	900	0.021360	0.004209	19.7	
PFR	0	300	0.013881	0.004689	33.8	
		700	0.014427	0.005010	34.7	
			0.013556	0.004717	34.8	Duplicate
	10	700	0.013486	0.004553	33.8	
	21	300	0.013447	0.004108	30.5	
		700	0.013447	0.004378	32.6	
		900	0.013853	0.004564	32.9	
			0.013318	0.004447	33.4	Duplicate
PFR w/Cu	0	900	0.022780	0.005374	23.6	

4.3 Detailed Brominated Flame Retardant Combustion Byproducts Analysis

Product yields

The major products generated at each temperature for each material are readily identified by GC-MS analysis. However, because the samples after pyrolysis or oxidation are so complex, additional analysis must be performed to examine the brominated byproducts constituents for each sample. Since analysis of the products using standards is difficult due to the fact that there is a thermal reactor in front of the GC-MS, the concentrations of the major compounds were estimated. At 300ºC in 0% oxygen atmosphere, the monobromophenol yield was estimated to be 1.2% of the mass of the board used. This estimate was calculated from the percentage of the laminate gasified (37% from Table 5), and the area percentage of chromatographic response from monobromophenol compared to the entire chromatographic run response (3.3%). The yield of the other major product (dibromophenol) was estimated to be 0.67% of the weight of the board exposed. These yields of the major products give an idea of the probable yield of the minor products.

The major products reported for the brominated flame retardants were the mono and dibrominated phenols. On the trace level (estimated as less than 1% of the total gaseous product mixture), a wide variety of compounds were formed as shown in Table 7. Various brominated aliphatic compounds were observed in small amounts, but the majority of compounds observed were brominated aromatics. Generally aromatic compounds are more stable, so this observation is appropriate.

Fate of brominated combustion byproducts

It is clear that some of the compounds reported for trace brominated organics were probably formed as products of incomplete combustion. This can be deduced because bromobenzene was not observed at 300ºC reactor temperature, but was observed in high amounts (on the trace level) at higher temperatures. We suspect that the bromophenols are relatively stable at 300ºC, but do degrade at higher temperatures to form bromobenzenes and in one case, trace amounts of bromobenzene diol. Even at reactor temperatures of 900ºC in an air atmosphere, there was some indication of the survival of these compounds through the reactor. At 900ºC, the four brominated compounds that could be observed were bromobenzene, bromobenzene diol, monobromophenol and dibromophenol. Blank runs (no sample) were conducted between analyses for many of the samples, and specifically between the 700ºC oxidation experiment and the 900ºC oxidation experiment. None of the major or minor compounds were observed in these blank experiments.

Even trace concentrations of brominated compounds were a surprise at these conditions. Oxidation at 900ºC should have been sufficient to completely oxidize the entire sample. It could be explained as follows: The sample was gasified instantaneously using pyroprobe. Because the amount of gas generated was relatively large compared to the carrier gas, it might have created oxygen deficit environment locally, and also there might not be enough time for gasified sample to be mixed with oxygen. Less surprising was the survival of the bromobenzene and the bromobenzene diol which were not present at temperatures of 300ºC and were present at 700 and 900ºC experiments. These clearly were formed as products during their time in the reactor, and the degradation of these compounds was not completed by the time these compounds escaped the high temperature reactor. From all this, we have learned that even at 2 seconds residence time in an air atmosphere, there is a small amount of bromine which will not be converted to HBr. The great majority of the brominated compounds, at these high temperatures, do convert to HBr. However, on the trace level, there is good evidence that compounds are surviving the exposure. This experimental system, because of its small sample size and short sampling time are not appropriate to observe the formation of brominated dibenzodioxins and brominated dibenzofurans. These types of compounds will be investigated in the larger scale systems.

Table 7 Identified Brominated Byproducts

		Area counts (x10E-06) from the Total Ion Current for each compound							
		pyrolysis (N2 atmosphere)				oxidation (21% O2 atmosphere)			
MW, g/mol	compound	300	700	900	blank	300	700	900	blank
		2-1-2	2-1-4	2-18-3	2-18-2	4-3-2	4-3-4	4-3-6	4-3-5
120	Br propene	**4.9**	ND	ND	ND	**0.2**	**0.1**	ND	ND
122	Br propane	**1.0**	ND	ND	ND	ND	ND	ND	ND
136	Br butane	**25.5**	ND	ND	ND	**6.6**	ND	ND	ND
172	Br phenol	**101.0**	**84.0**	ND	ND	**130.0**	**147.0**	**31.1**	ND
250	Br2 phenol	**55.0**	**27.7**	ND	ND	**93.0**	**69.6**	**7.5**	ND
206	Br naphthalene	ND	ND	ND	ND	ND	ND	ND	ND
262	Br dibenzodioxin	ND	ND	ND	ND	ND	ND	ND	ND
246	Br dibenzofuran	ND	ND	ND	ND	ND	ND	ND	ND
156	Br benzene	**0.1**	**4.7**	ND	ND	ND	**14.0**	**10.0**	ND
234	Br2 benzene	ND	**0.0**	ND	ND	ND	**1.1**	**1.4**	ND
214	Br propyl phenol	**3.5**	**3.4**	ND	ND	**14.0**	**0.1**	**0.2**	ND
292	Br2 propyl phenol	ND	ND	ND	ND	ND	ND	ND	ND
290	Br2 propenyl phenol	**2.3**	ND	ND	ND	**2.1**	ND	ND	ND

4.4 Phosphorous Flame Retardant Combustion Byproducts Analysis

With regard to phosphorous-containing trace organic compounds, we were not able to observe, even on the trace level, any phosphorus containing organic compounds. Several different phosphorous compounds were selected which were aromatic phosphorus containing compounds, including phenylphosphine, dimethyl phenylphosphine, phenylphosphinic acid, C3 phenyl phosphine, phenylphosphonic acid, hydroxyphenylphosphonic acid, and C4 phenylphosphine. The major ions from these compounds were checked for the phosphorous containing laminate materials, and none of these compounds were observed, even on the trace level.

The literature suggests that radical capture is not the mechanism of flame retardancy in phosphorous containing materials as it is with the brominated materials. Levchik and Weil[1] report some good information about these flame retardant materials. In our sample, we suspect that a aminophenyl phosphorous compound was used in the formulation as we do observe, on a trace level, the compound aniline as one of the compounds formed at 300ºC. Since many of the phosphorous retardants work by forming phosphate on the surface of the material they are protecting and “crusting” up the surface, we would expect aromatic formation from phenyl groups in the flame retardant formulation and the phenol degradation to take place. We do observe more polycyclic aromatic hydrocarbon (PAH) formation in this retardant than in the brominated retardant. The mechanism by which phosphorous FRs retard flame (surface complexes and PO_2 interaction with H/OH) prohibits incorporation of phosphorus with stable organic compounds. Thus, the phosphorous compounds could not be observed downstream of the reactor.

4.5 Hydrogen Chloride Analysis

During the course of experiments we were informed by the EPA that at least some (if not all) of the samples contained chlorine. Standard epoxies used for the laminate contain 1000 to 2500 ppm (0.1 to 0.25 wt %) chlorine. Therefore, we also examined if exhaust gas contained hydrogen chloride. Hydrogen chloride was found from brominated flame retardant pyrolysis and combustion tests, and phosphorus flame retardant pyrolysis tests. No hydrogen chloride was found from non-flame retardant pyrolysis and combustion tests. We did not look for chlorinated organics, such as polychlorinated dibenzodioxin, in these samples as there was an extremely low possibility of forming these organics at measurable levels with a flow reactor..

4.6 Aqueous Sample Analysis

The aqueous samples collected from combustion tests of BrFRs (w/o Cu) at 900ºC with 21% oxygen, and pyrolysis of BrFRs (w/o Cu) at 900ºC, were analyzed for bromine ion concentration. Results are shown in Table 8 and Figure C1 and C2 in Appendix C.

The samples were analyzed using a colorimetric method called Flow Injection Analysis (FIA)[2,3]. In this analysis, bromine ions react with reagents to form a colored complex which absorbs at 590 nm. The absorbance measured at 590 nm is directly proportional to the bromine ion concentration of the sample. Standards of 1, 2, 5, and 10 ppm are used for comparison to the sample solutions ($R^2 = 0.9995$). Figures C1 and C2 show the results of these two analyses. The sample labeled Blank 30 did not generate a peak as would be expected. The sample labeled BrFRCuP -1 (bromine flame retardant with Cu laminate) produced a negative peak, which was observed in both runs. It is believed that some other ion in the sample matrix may have reacted with method reagents to create a colored complex with a lower absorbance than the carrier solution. A TIC taken at the same time (Figure B9) also showed no HBr and no other brominated compounds. It is possible that Br reacted with copper in the pyroprobe to form $CuBr_2$, and it could have been condensed elsewhere on the reactor wall and transfer line. The aqueous samples from the Br flame retardant without Cu laminate showed bromine ion in it. Based on the XRF analysis, averaged Br concentration in the flame retardant sample was 6.17%. The expected Br ion concentration from two brominated flame retardant combustion tests were 14.0 and 13.8 ppm if all bromine converted to HBr. 63 and 51% bromine was recovered as HBr from the aqueous samples. The TIC taken at the same time (Figure B21 and B22) also consistently showed a large HBr peak.

Table 8 Aqueous sample analysis for Br ion concentration

Sample	**Br Ion Concentration (ppm)**	
	Run 1	Run 2
Br flame retardant w/o Cu 1st run (BrFR921-1)	8.77	8.87
Br flame retardant w/o Cu 2nd run (BrFR921-2)	7.06	7.14
Br flame retardant w/ Cu (BrFCuP1)	Not detected	Not detected

After the flow reactor combustion test, Br transport efficiency test was conducted using tetrabromobisphenol A (TBBPA) (Aldrich, St. Louis, MO) as a Br source. TBBPA was dissolved into methylene chloride and dried in the quartz cartridge that was used for sample gasification. TBBPA was gasified in same manner as PCB samples. Reactor temperature was set at 700ºC, and gasified TBBPA was carried by N2 through reactor at the residence time of 2 sec. Sample was purged through a 40cc vial that contained 20cc HPLC grade ultrapure water. Results were summarized in Table 9. Br recovery rate was 33.2%. At 700ºC TBBPA will most likely decompose to HBr, or dissociated Br atom may react with the quartz reactor tube. The surface analysis and/or extraction of the reactor and transport line between reactor and vial could be further performed to elucidate the Br recovery rate if funding situation allows us to do so. Also our water impinger may not be sufficient to capture all HBr.

Table 9 Br transport test using TBBPA as a Br source

Sample	Br Introduced as TBBA (mg)	Expected Br if all Br converted to HBr (ppm)	Br recovered from aqueous sample (ppm)	Recovery Rate as Br (%)
TBBPA	0.393	11.5	3.82	33.2

5. Literature Review and Comparison

Relevant literature data for Br flame retardant circuit board and TBBPA pyrolysis and combustion experiments was reviewed after the experiment to better understand our experimental results. Grause et al.[4] conducted the pyrolysis of TBBPA containing paper laminated printed circuit board (PCB). The major constituents and their wt% of TBBA containing PCB are C (57.0%), H (6.3%), and Br (3.64%). The sample was pyrolised in a quartz glass reactor. The sample was heated from 50 to 800ºC with a heating rate of 10K/min. and a N2 flow of 100mL/min. The volatile products were gathered in four gas washbottles each containing 50mL of methanol. HBr content was determined by ion-chromatography (IC), and organic products were analyzed by GC-MS. Methylated phenols and methylated benzene derivatives were the most prominent degradation products after phenol. Also brominated phenols were found among the degradation products of TBBA, with main products being 2-bromophenol, 2,4- and 2,6-dibromophenols, and 2,4,6-tribromophenol. Most of the bromine was released in the form of HBr (87%), another 14% was bound in organic compounds, and about 1.8% of original bromine content was left in the residue. The release of the brominated aromatics was completed below 400ºC. However, only 50% of the bromine was released as HBr at this temperature. Another 37% of HBr was released from the resin between 400 and 700ºC. Barontini et al.[5,6] investigated thermal decomposition products and decomposition pathways of electronic boards containing brominated flame retardants using thermogravimetric (TG) FTIR and laboratory-scale fixed bed tubular batch reactor coupled with GC-MS/FID. The major constituents and their wt% are C (22.1~27.4%), H (2.0~2.4%), and Br (6.0~ 6.9%). The degradation products identified includes non-brominated aromatics (phenol, biphenyl, anthracene/phenanthrene, dibenzofuran, dibenzo-p-dioxin, bisphenol A), brominated benzene, phenols, and dibenzofurans and dioxins. Chien et al. [7] studied behavior of Br in pyrolysis of the printed circuit board waste. Pyrolysis of the printed circuit board wastes was carried out in a fixed bed reactor at 623-1073K for 30 min. in N_2. Condensable product gases were analyzed using FTIR, and non-condensable gases were scrubbed with NaOH solution. The main constituents and their wt% are C (52.2%), H (6.11%), Br (8.53%), and copper (9.53%). Approximately 72.3% of total Br in the printed circuit board waste was found in product gas mainly as HBr and bromobenzene. Cu-O and Cu-(O)-Cu species were observed in the solid residues. No Cu-Br species was found in the solid residue. Barontini et al.[8,9] also conducted TBBPA decomposition product analysis. The analytical technique applied was similar to the one they conducted for Br flame retardant containing electronic boards. Major products formed were HBr, phenol, mono, di, and tribromophenols, bisphenol A, and brominated bisphenol A.

Our results show small amount of HBr for brominated flame retardant pyrolysis at 700ºC, and oxidation with 21% O_2 at 300ºC, and large amount of HBr for the oxidation with 10 and 21% O_2 at 700ºC and 21% O_2 at 900ºC. Our HBr recovery rate could have been greater, if multiple series of impingers and more water were used. Also if samples were captured using methanol impingers and analyzed using GC-MS as Grause et al. performed, instead of cryogenical trap, more brominated organic could have been identified, even though we had also identified many brominated organic compounds at the trace level. Experimental setup and analytical procedure will be reconsidered and redesigned for Phase II experiment for the better sample identification and bromine mass balance.

6. Conclusions

In this work, the controlled thermal exposure of flame-retardant and non-flame retardant laminates was examined. Results for brominated flame retardant laminates showed that bromophenol and dibromophenol were the main brominated organic products, with estimated yields of 1.2% for methylbromophenol and 0.67% for the dibromophenol. The responses for methylbromophenol and Dibromophenol decreased with increasing temperature, and were below detectable levels for oxygen free experiments. However, oxidation experiments indicated that even at 900ºC, some amounts of organic bromine containing compounds survived. In addition, bromobenzene and substituted bromophenols were formed at high temperatures, even though they were not formed at the 300ºC exposure (in both oxidation and pyrolysis). It is possible that these bromophenols and bromobenzenes will be sources for the formation of products in the cone calorimeter experiments, such as dioxins and furans.

Organic phosphorus compounds were not observed in the reactor exhaust gases during phosphorus FR experiments. When phosphorus containing flame retardants are used, the product distribution is similar to the non-flame retardant laminate experiments, in that there is a wide variety of polycyclic aromatic hydrocarbons (PAHs) such as benzene, toluene, xylene, and naphthalene. The results from this study suggests that cone calorimeter experiments will generate a large amount of PAH type compounds for all of the laminate systems but that the brominated system is likely to yield brominated dioxins and furans because of the relatively high yields of brominated phenols observed at high temperatures in this study. In addition, the compounds we should expect in the cone calorimeter are higher yields of methylbromophenol, dibromophenol, bromobenzene (mono and di) as well as brominated and nonbrominated fragments of bisphenol A, such as C_3 substituted bromophenol, bromomethylphenol and the like. All of the laminates formed large amounts of phenol and alkyl substituted phenols.

These experiments did not use enough mass of laminate to perform dioxin and furan analysis on-line. The investigation of these compounds should be performed with larger masses of sample and using off-line analysis as it is being performed for the cone calorimeter experiments. The lab scale experiments indicate that even under well controlled conditions, it is difficult to completely degrade the brominated phenols, even at 900ºC. While most of the bromine is converted to HBr, its conversion is not complete unless very well controlled mixing is available to expose all of the gaseous products to 21% oxygen.

References:

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9. Barontini, F.; Marsanich, K.; Petarca, L.; Cozzani, V. Ind. Eng. Chem. Res. 2004, 43, 1952-1961.

Appendix A
Thermogravimetric Analysis (TGA)

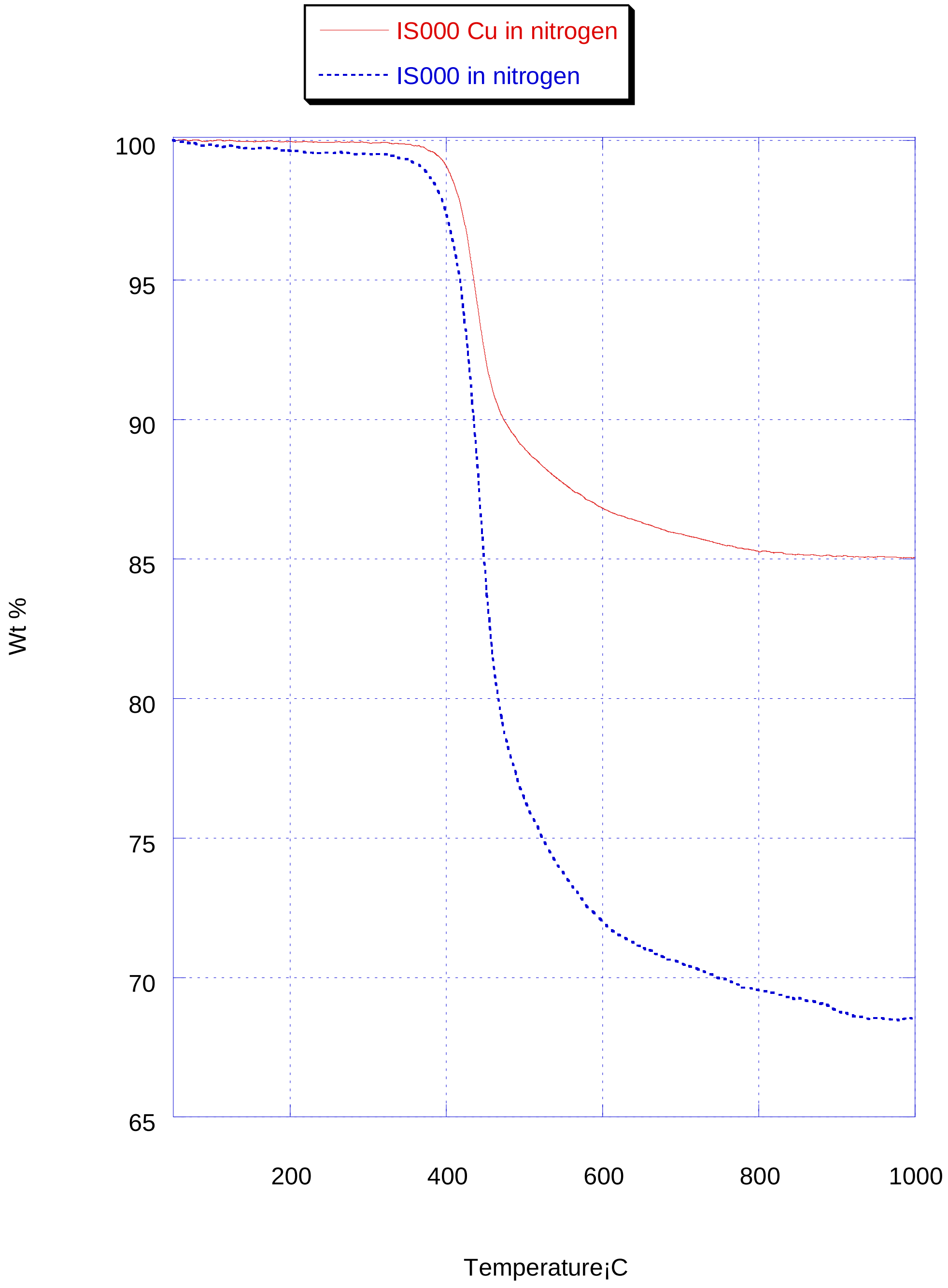


Figure A1. TGA in N_2 for Non-flame Retardant Sample with and without Cu Laminate

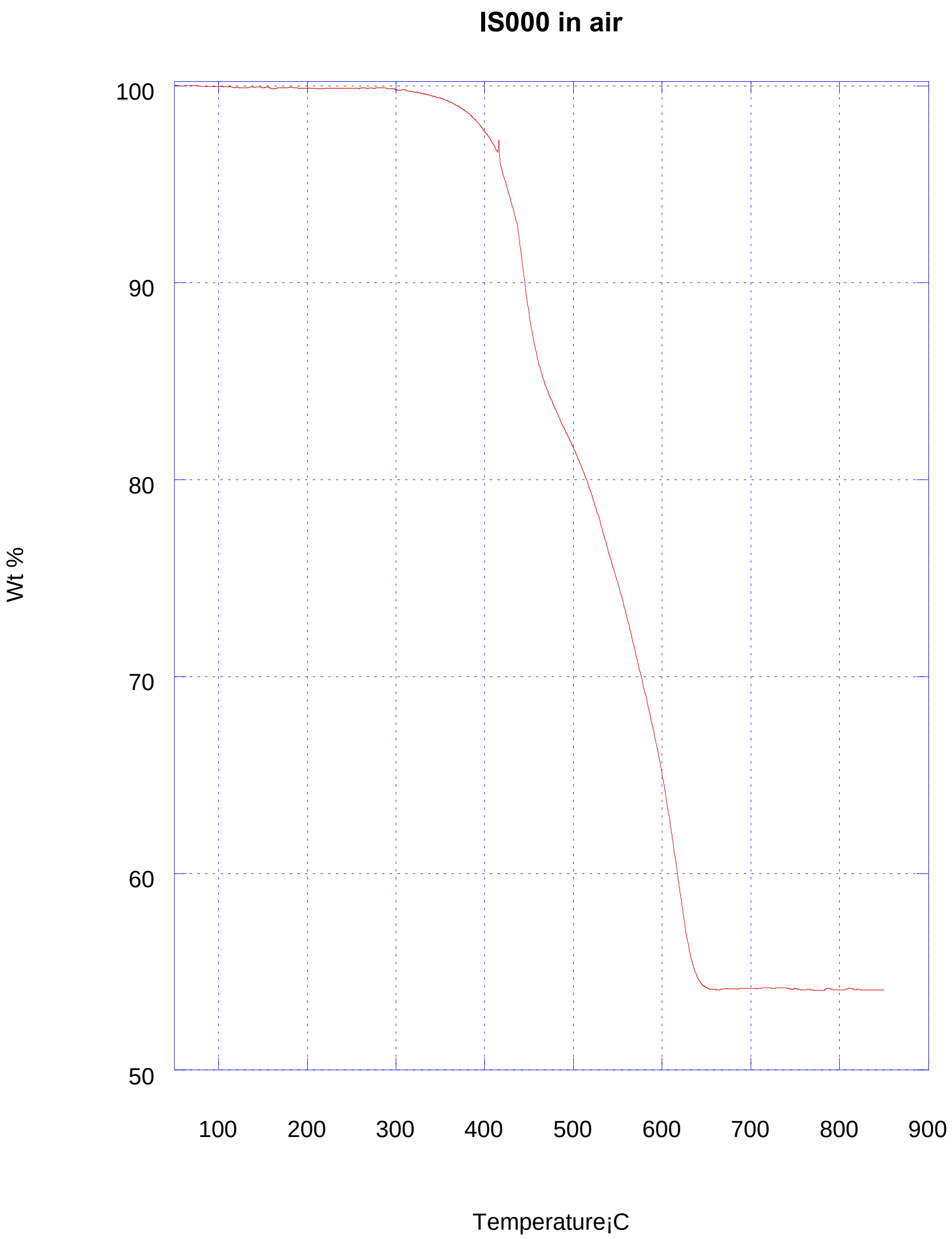


Figure A2. TGA in Air for Non-flame Retardant Sample without Cu Laminate

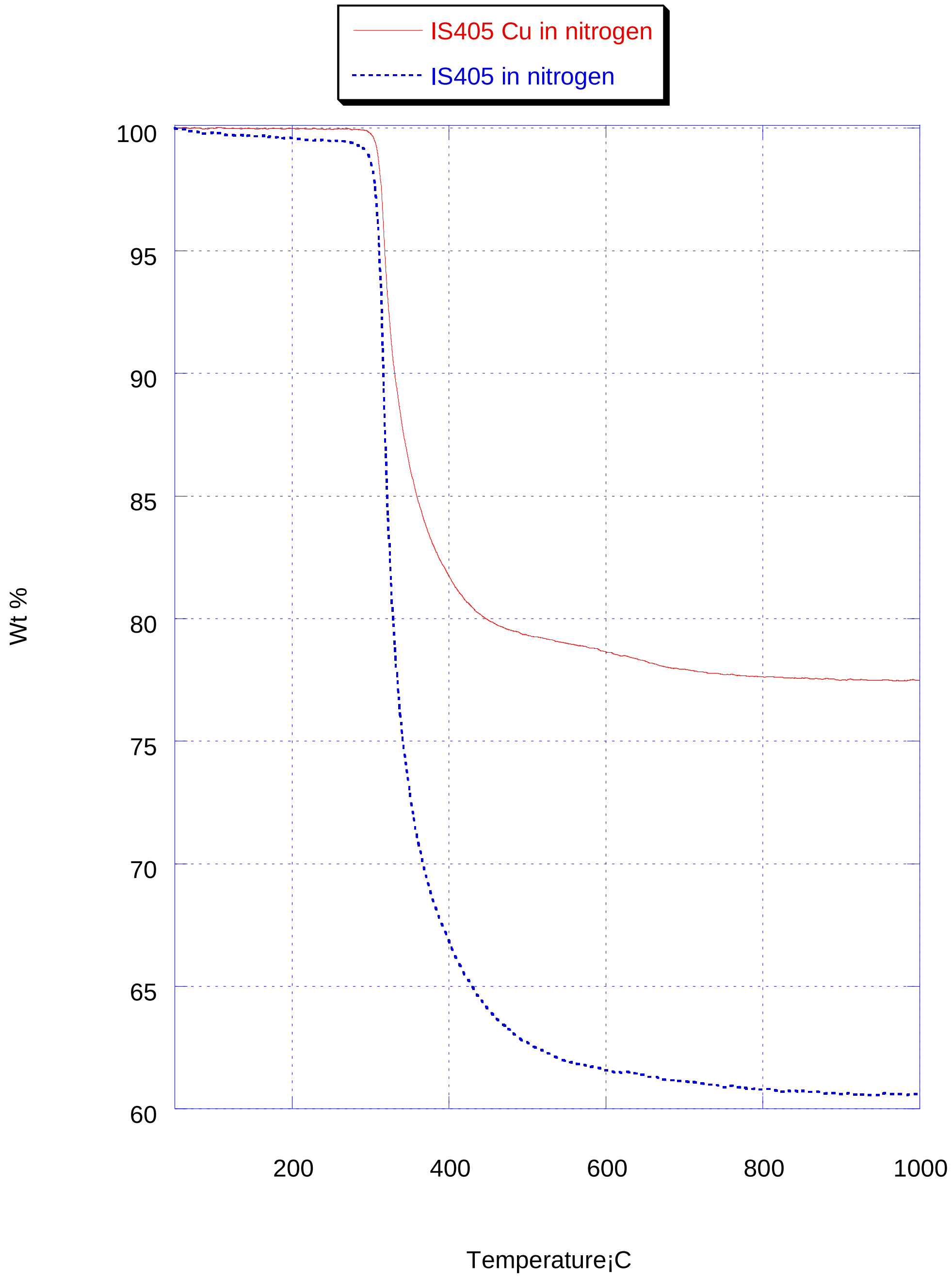


Figure A3. TGA in N_2 for Brominated Flame Retardant Sample with and without Cu Laminate

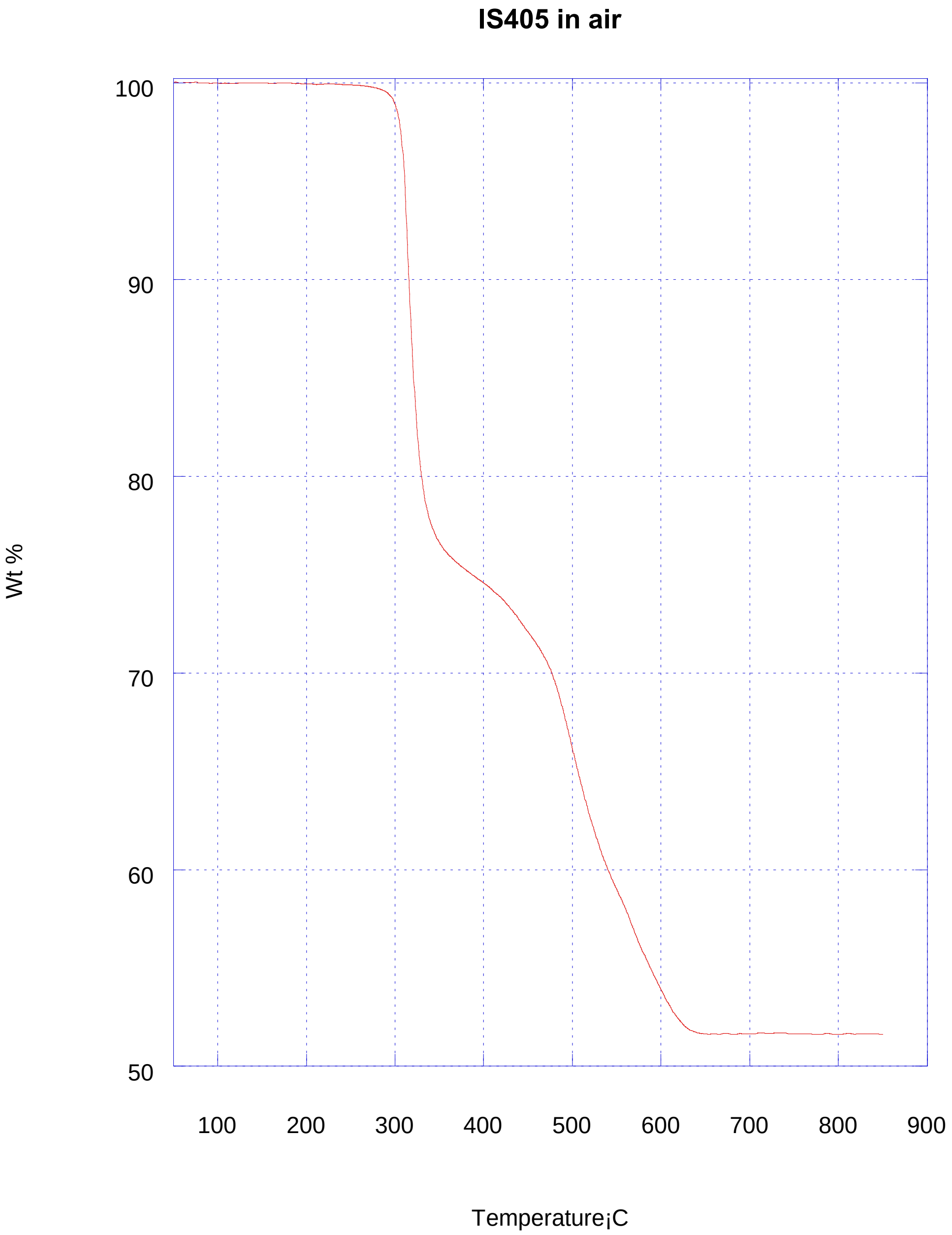


Figure A4. TGA in Air for Brominated Flame Retardant Sample without Cu Laminate

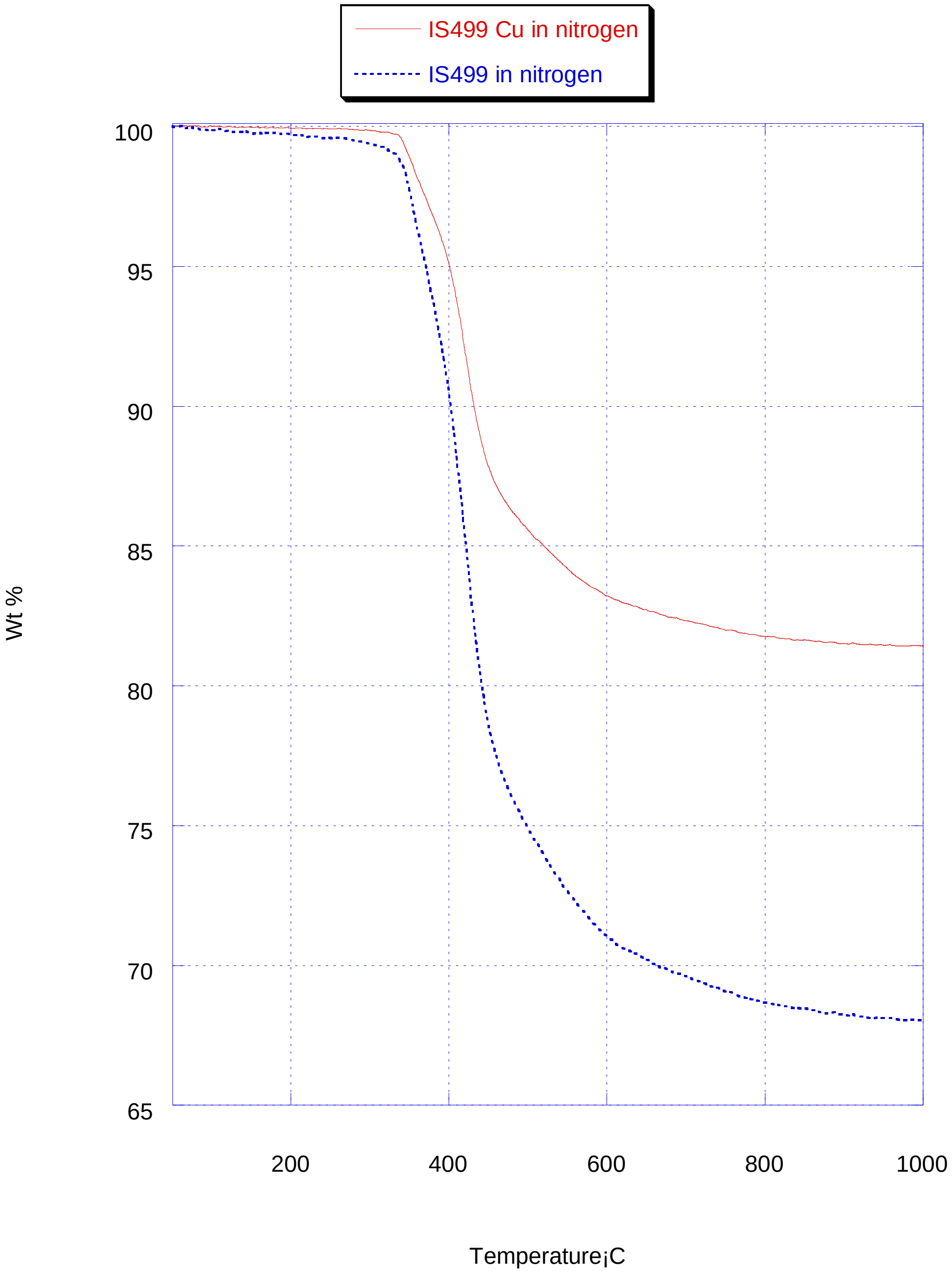


Figure A5. TGA in N_2 for Phosphorous Flame Retardant Sample with and without Cu Laminate

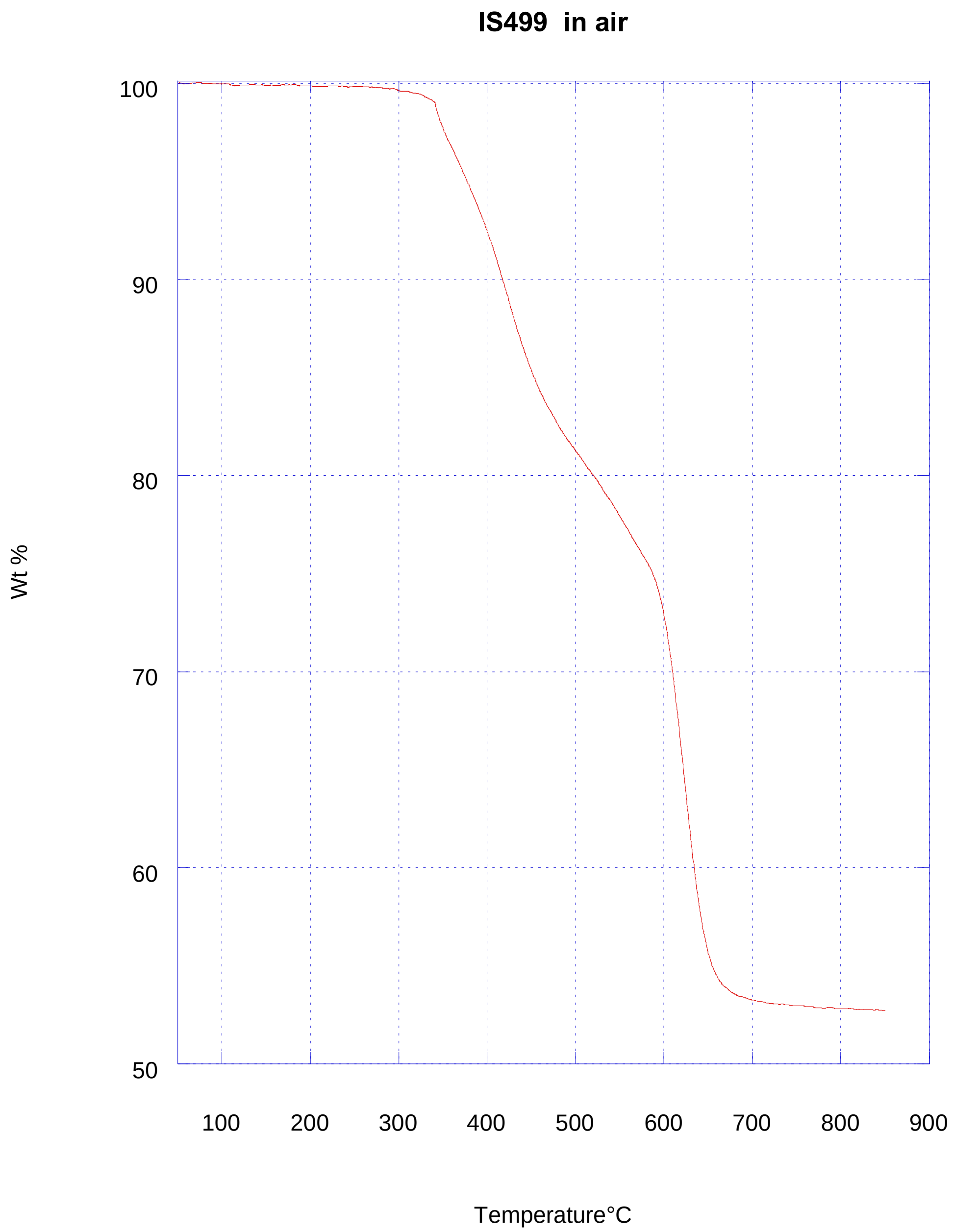


Figure A6. TGA in Air for Phosphorous Flame Retardant Sample without Cu Laminate

Appendix B
Total Ion Chromatogram Obtained from Circuit Board Combustion Byproducts Analysis

Table B1 Chemical Name – Structure Reference Table

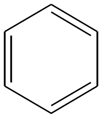
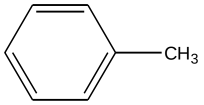
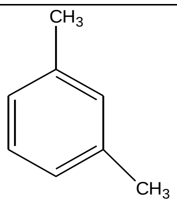
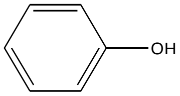
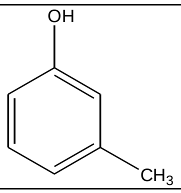
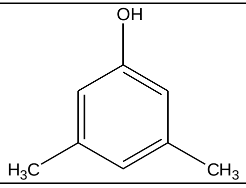
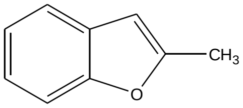
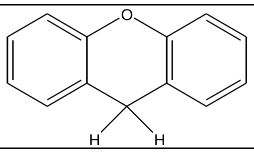
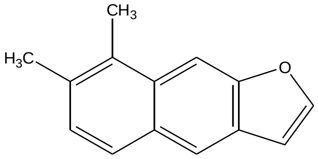
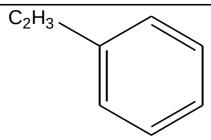
Chemical Name	Chemical Structure
Benzene	
Toluene	
Xylene (one of isomers)	
Phenol	
Methylphenol (one of isomers)	
Dimethylphenol (one of isomers)	
2-methylbenzofuran	
Xanthene	
1,2-dimethyl-naphthofuran	
Styrene	

Table B1 Chemical Name – Structure Reference Table (Cont'd)

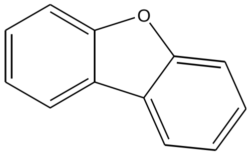
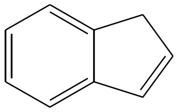
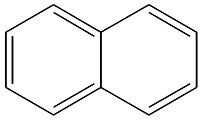
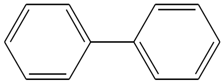
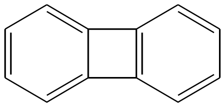
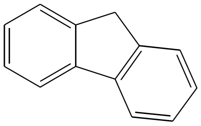
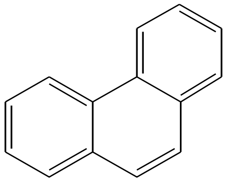
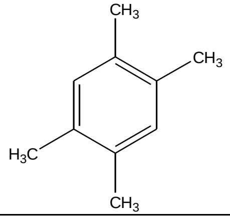
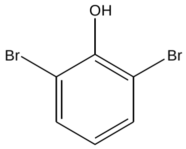
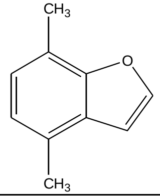
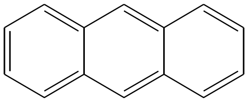
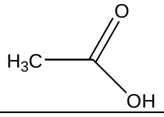
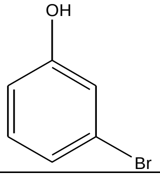
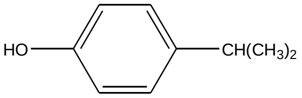
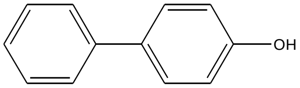
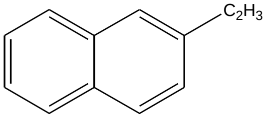
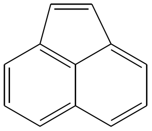
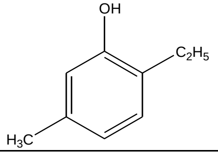
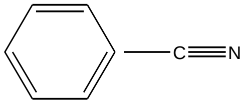
Dibenzofuran	
Indene	
Naphthalene	
Biphenyl	
Biphenylene	
Fluorene	
Phenanthrene	
Tetramethylbenzene (one of isomers)	
Dibromophenol (one of isomers)	
Dimethylbenzofuran (one of isomers)	

Table B1 Chemical Name – Structure Reference Table (Cont'd)

Anthracene	
Acetic Acid	
Bromophenol (one of isomers)	
Methylethylphenol (one of isomers)	
Hydroxybiphenyl (one of isomers)	
Ethenylnaphthalene (one of isomers)	
Acenaphthylene	
Methylethylphenol (one of isomers)	
Benzonitrile	

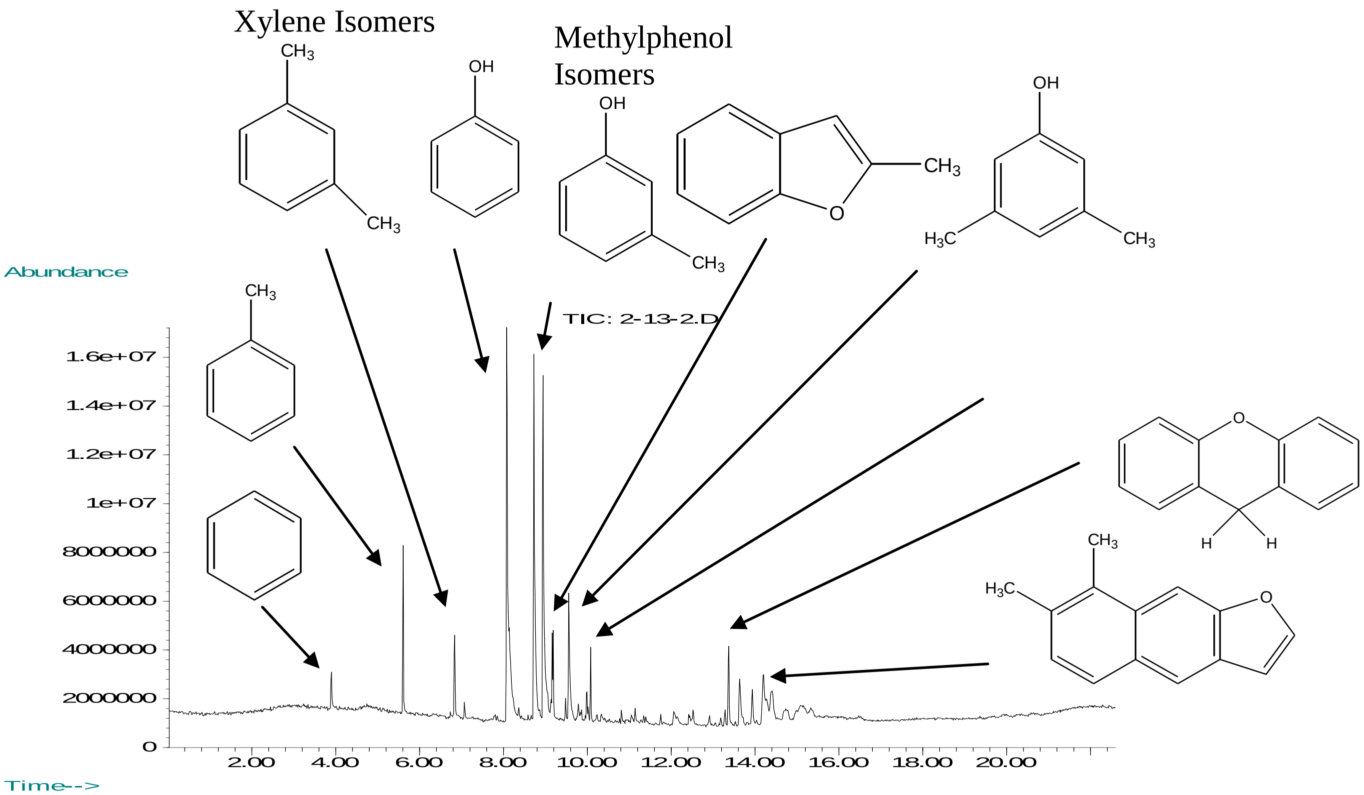


Figure B1. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under Pyrolysis Condition at 300°C

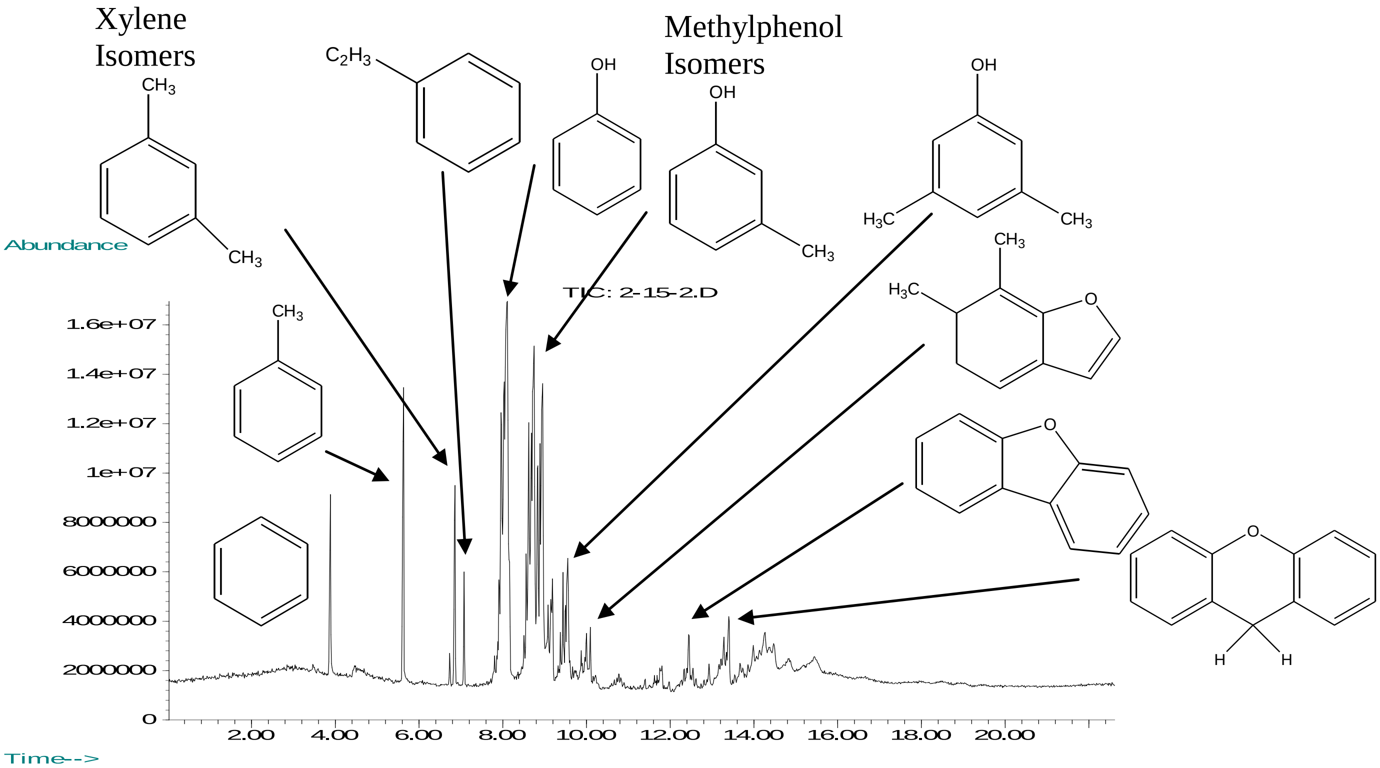


Figure B2. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under Pyrolysis Condition at 700°C

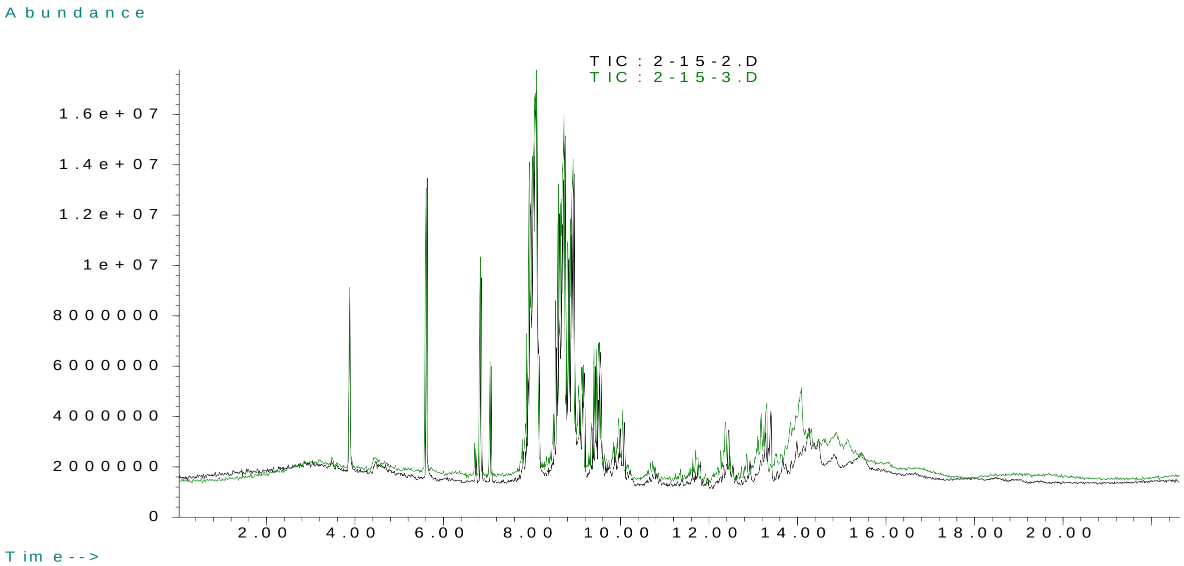


Figure B3. Overlaid TIC for Repeated Experiment (Non-flame Retardant Sample under Pyrolysis Condition at 700°C)

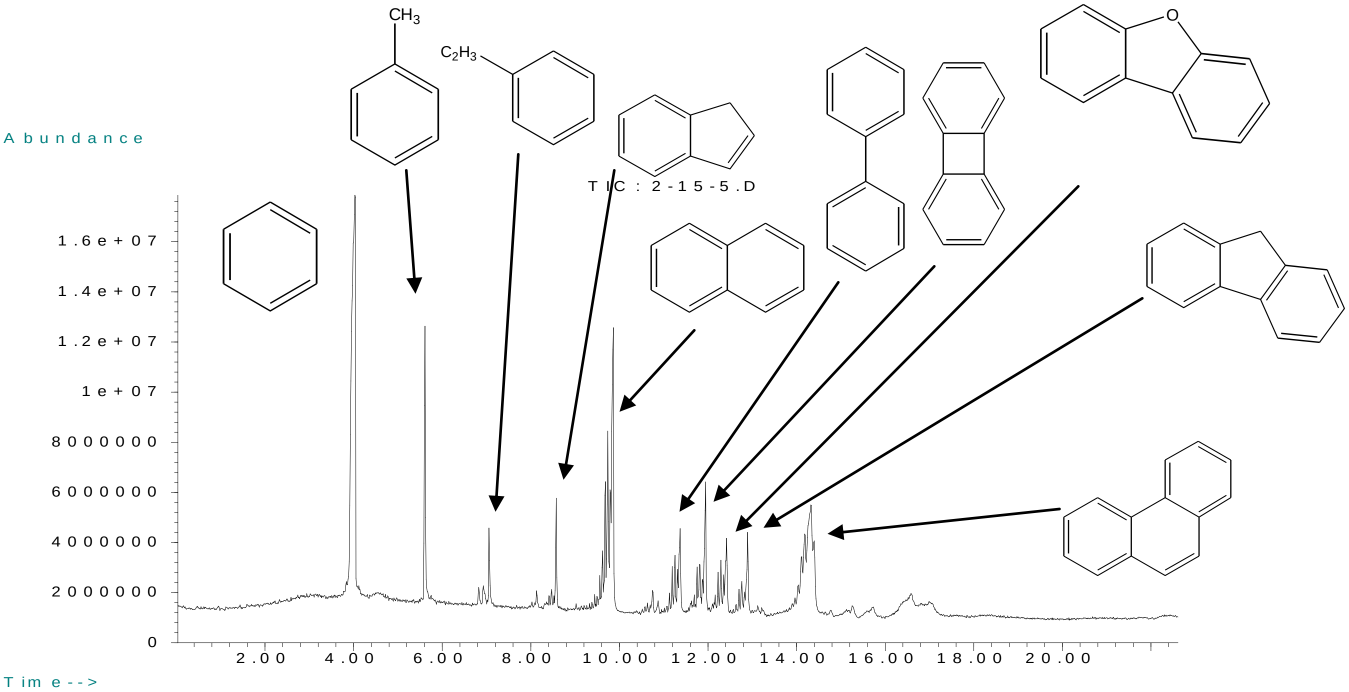


Figure B4. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under Pyrolysis Condition at 900°C

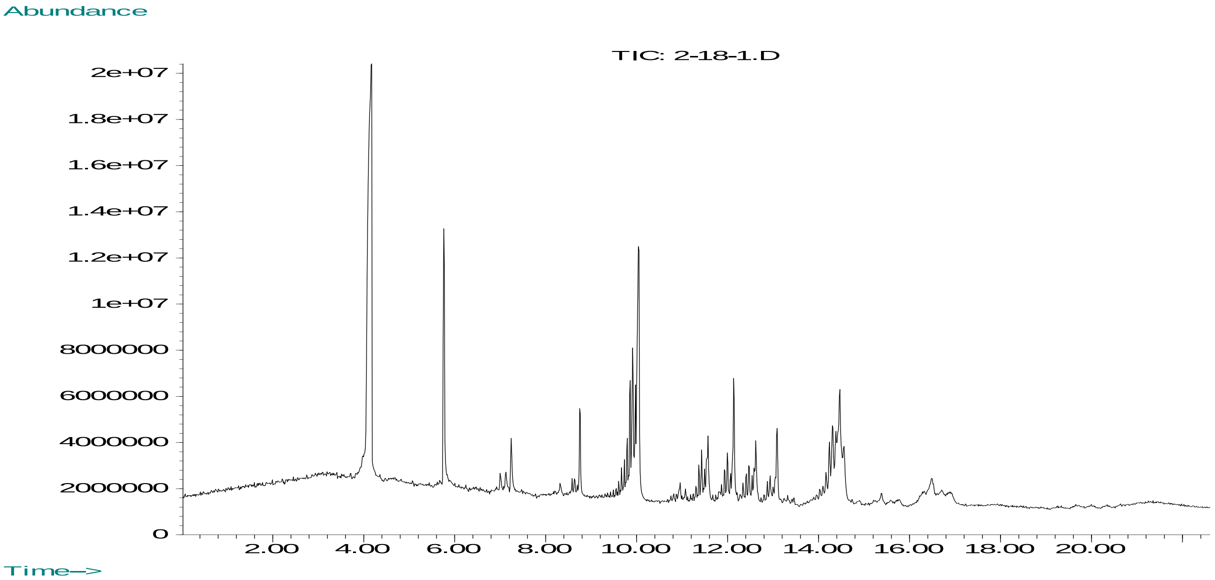


Figure B5. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample with Cu Laminate under Pyrolysis Condition at 900°C. Peak identifications are same as above (Figure B4).

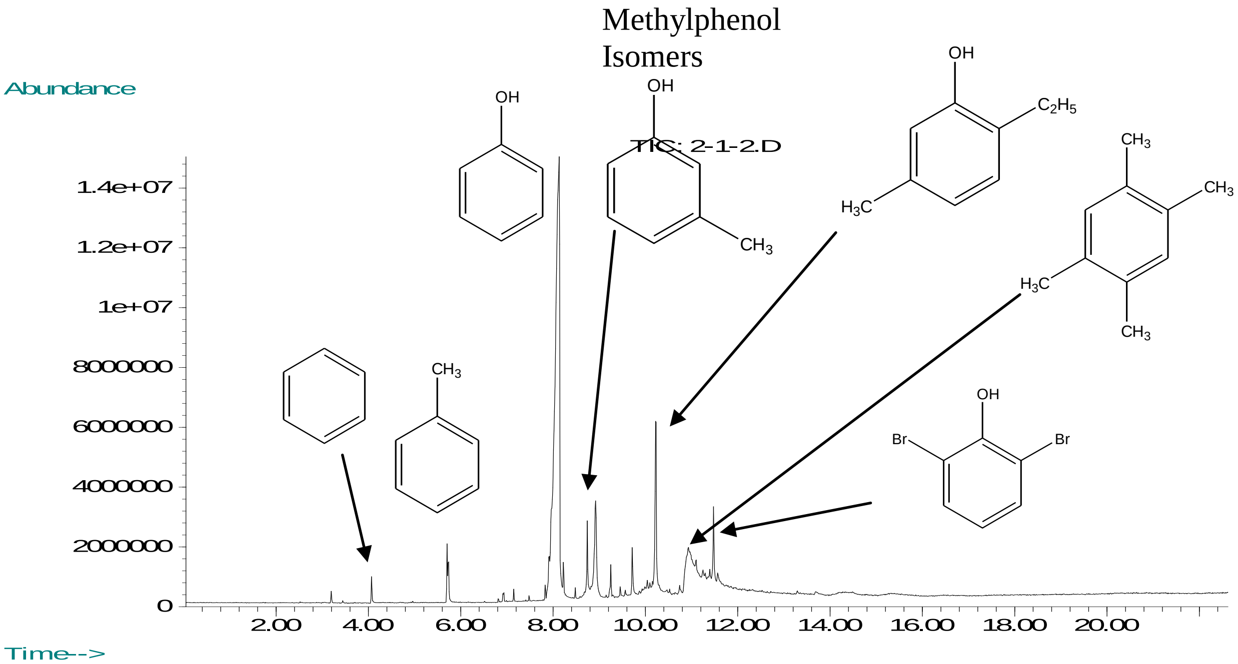


Figure B6. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under Pyrolysis Condition at 300°C

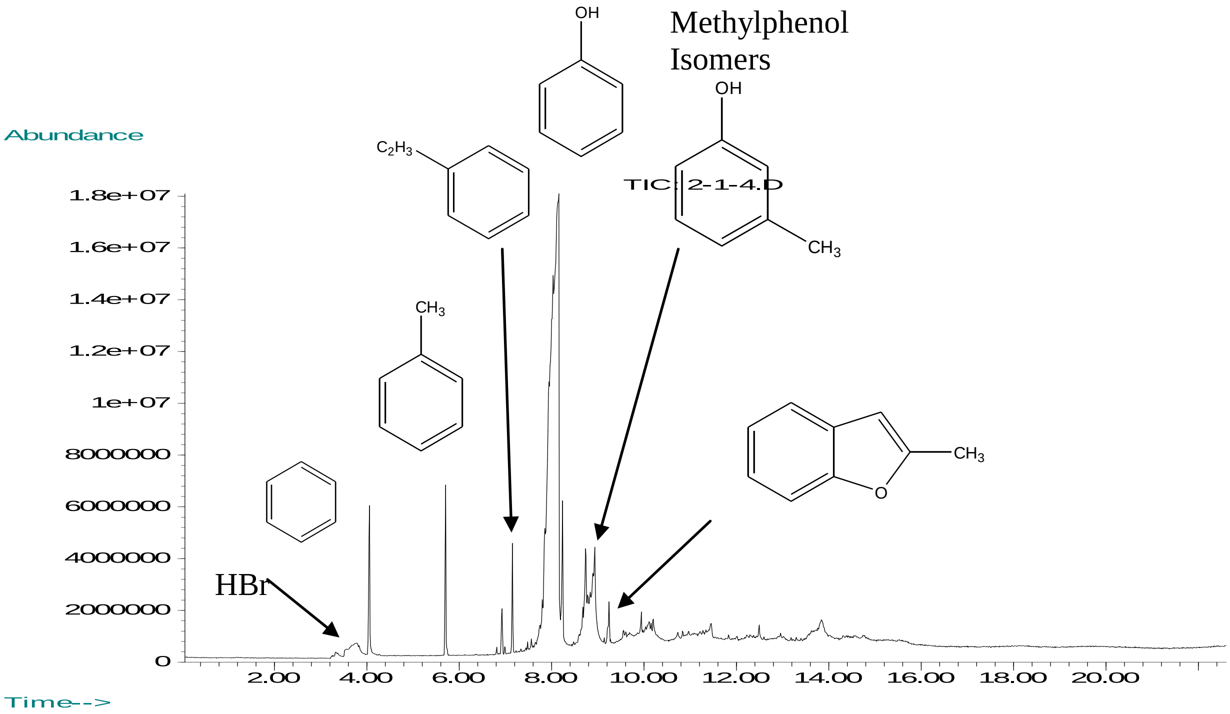


Figure B7. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under Pyrolysis Condition at 700°C

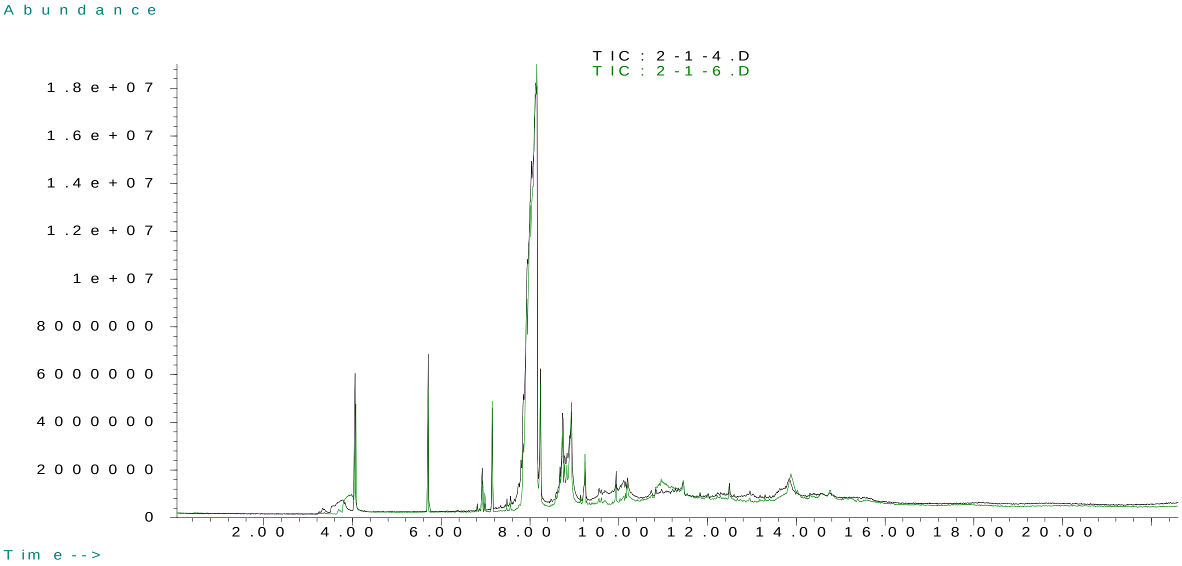


Figure B8. Overlaid TIC for Repeated Experiment (Brominated Flame Retardant Sample under Pyrolysis Condition at 700°C)

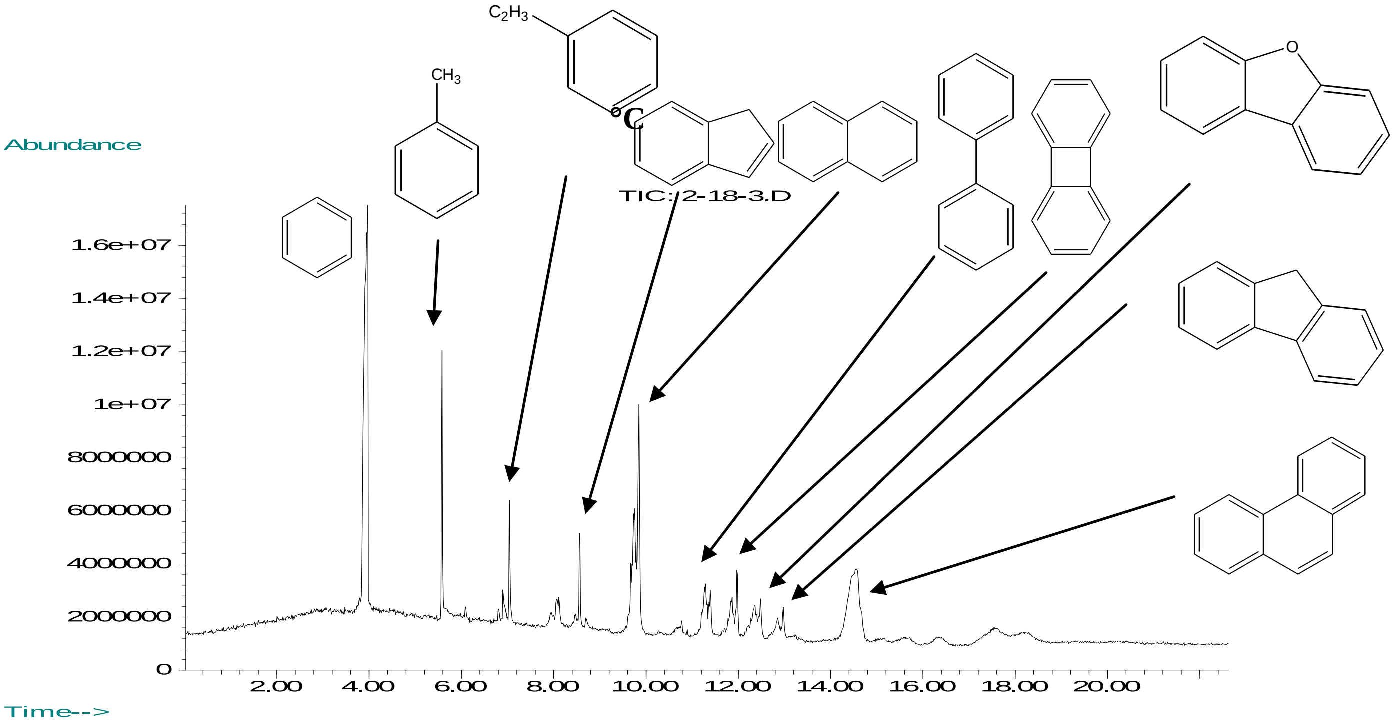


Figure B9. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample with Cu Laminate under Pyrolysis Condition at 900°C

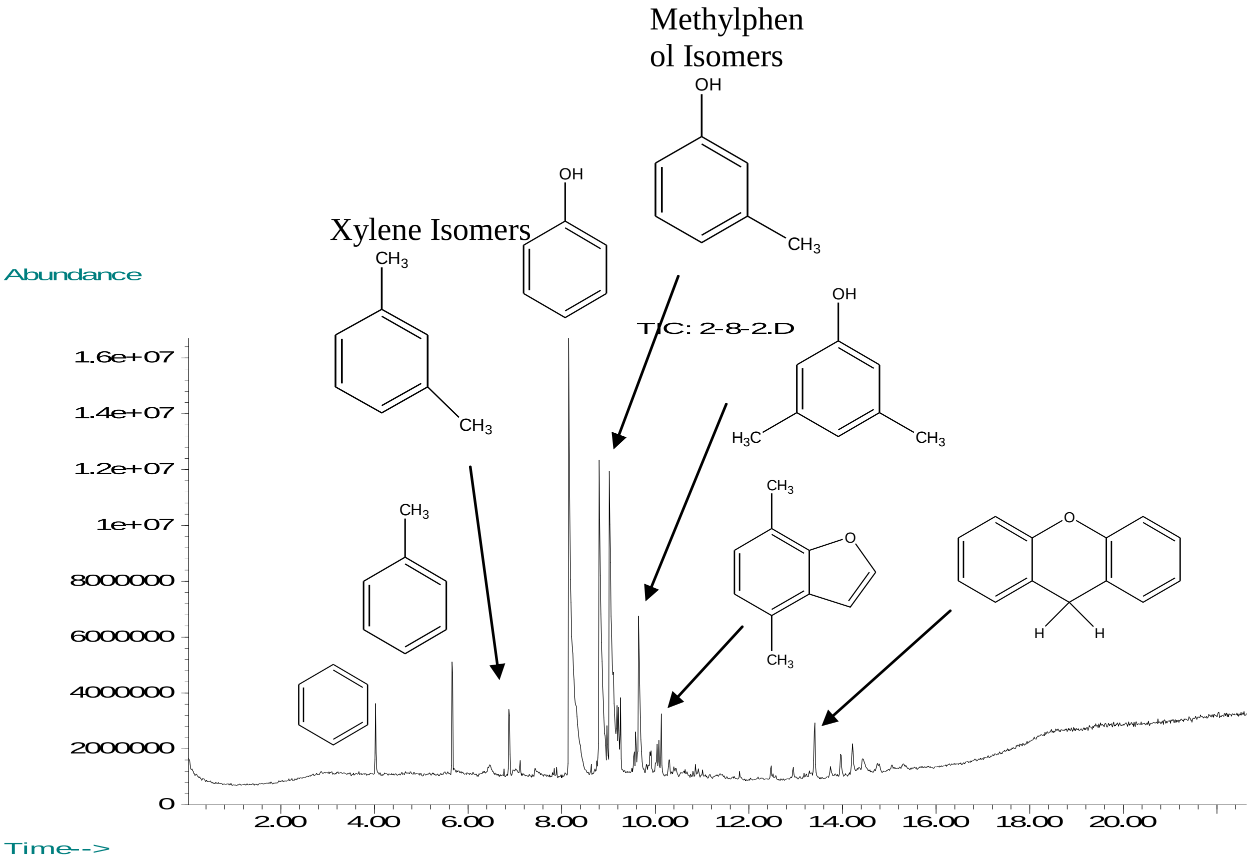


Figure B10. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under Pyrolysis Condition at 300°C

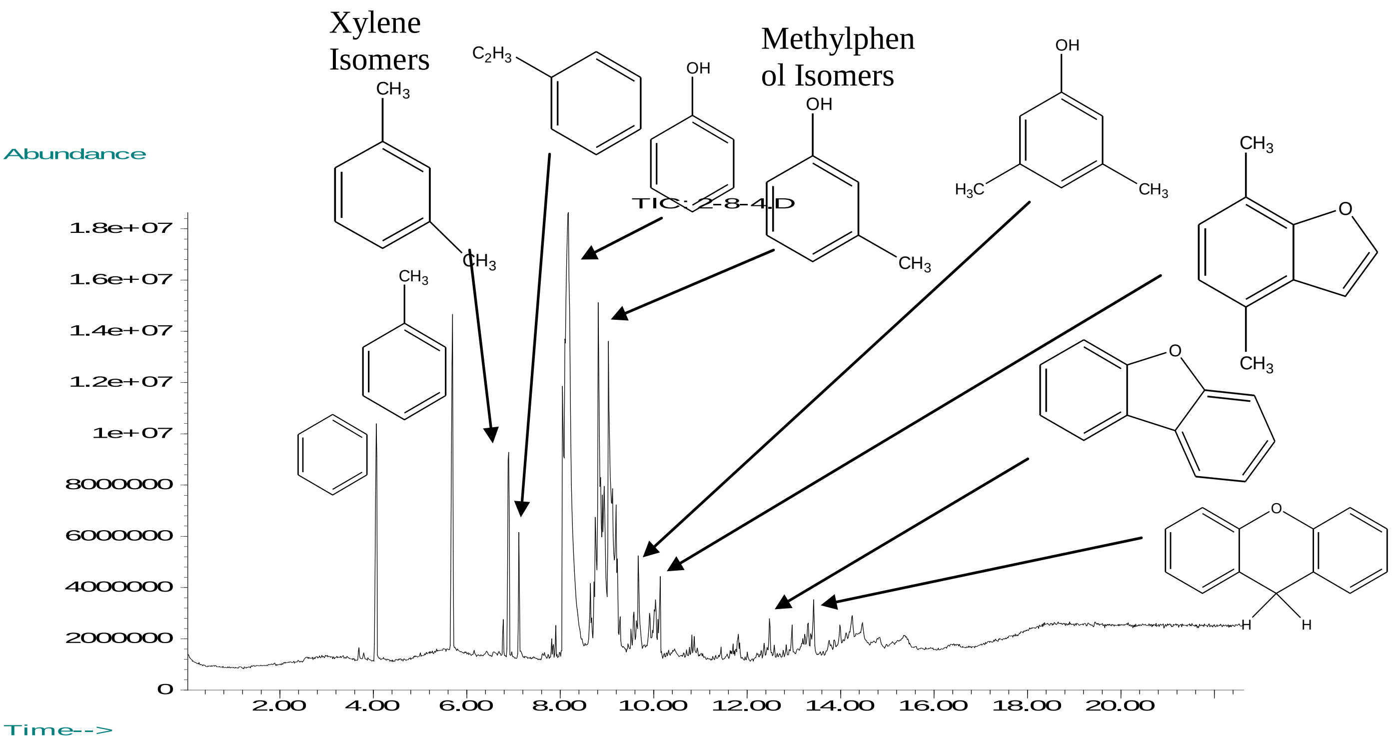


Figure B11. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under Pyrolysis Condition at 700°C

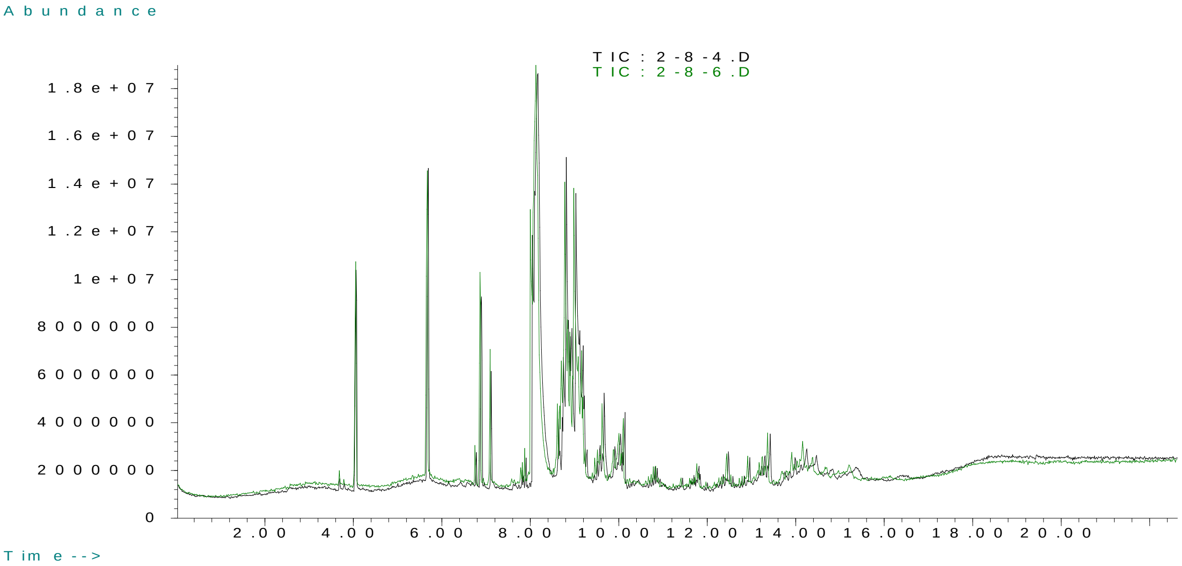


Figure B12. Overlaid TIC for Repeated Experiment (Phosphorous Flame Retardant Sample under Pyrolysis Condition at 700°C)

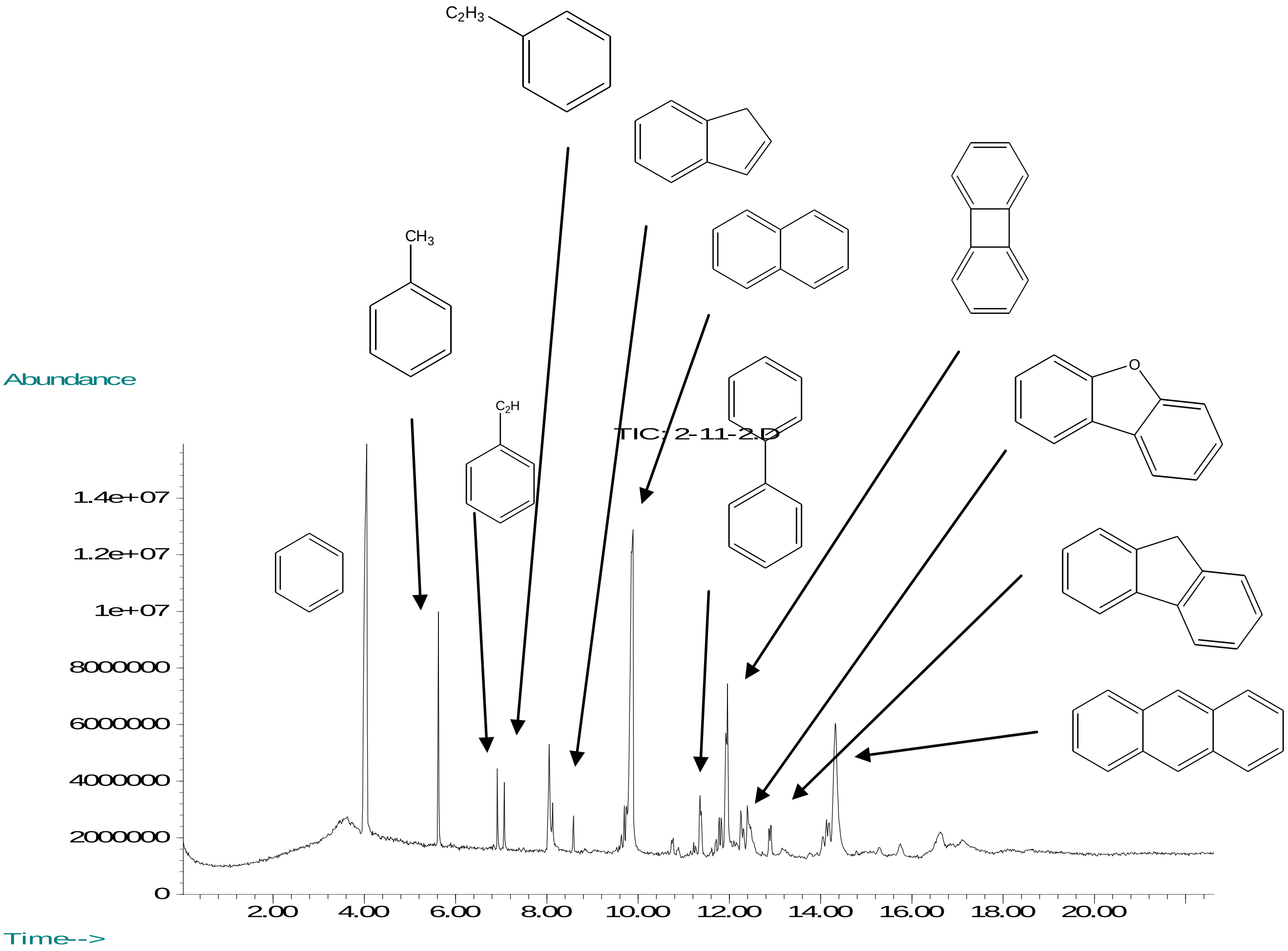


Figure B13. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample with Cu Laminate under Pyrolysis Condition at 900°C

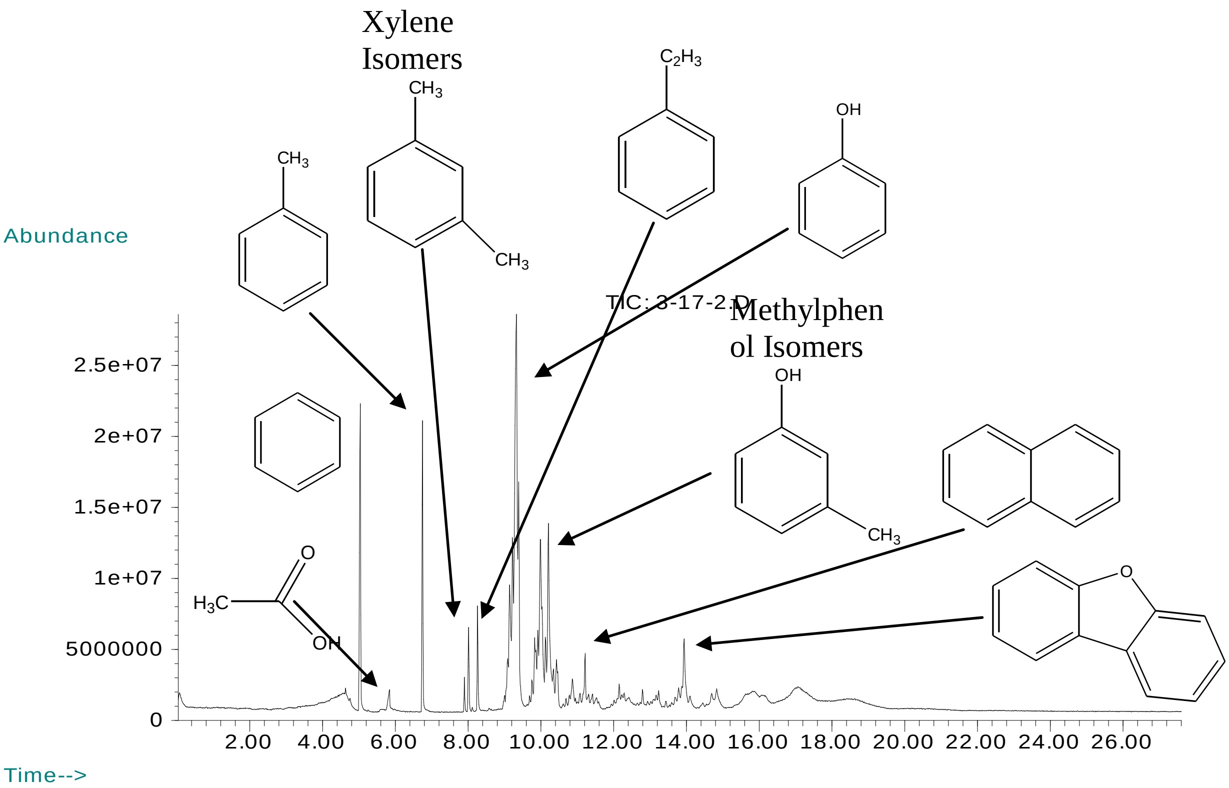


Figure B14. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under 10% O2 Condition at 700°C

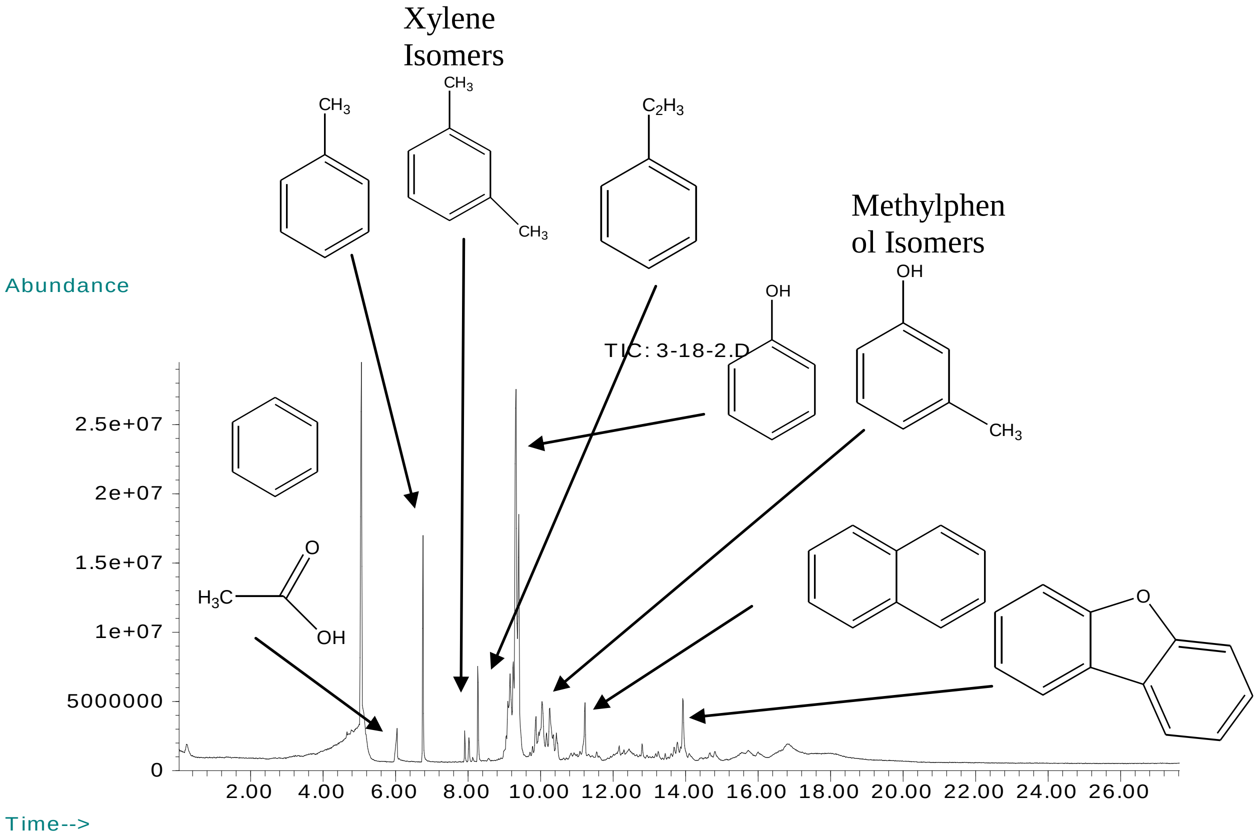


Figure B15. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under 21% O2 Condition at 700°C

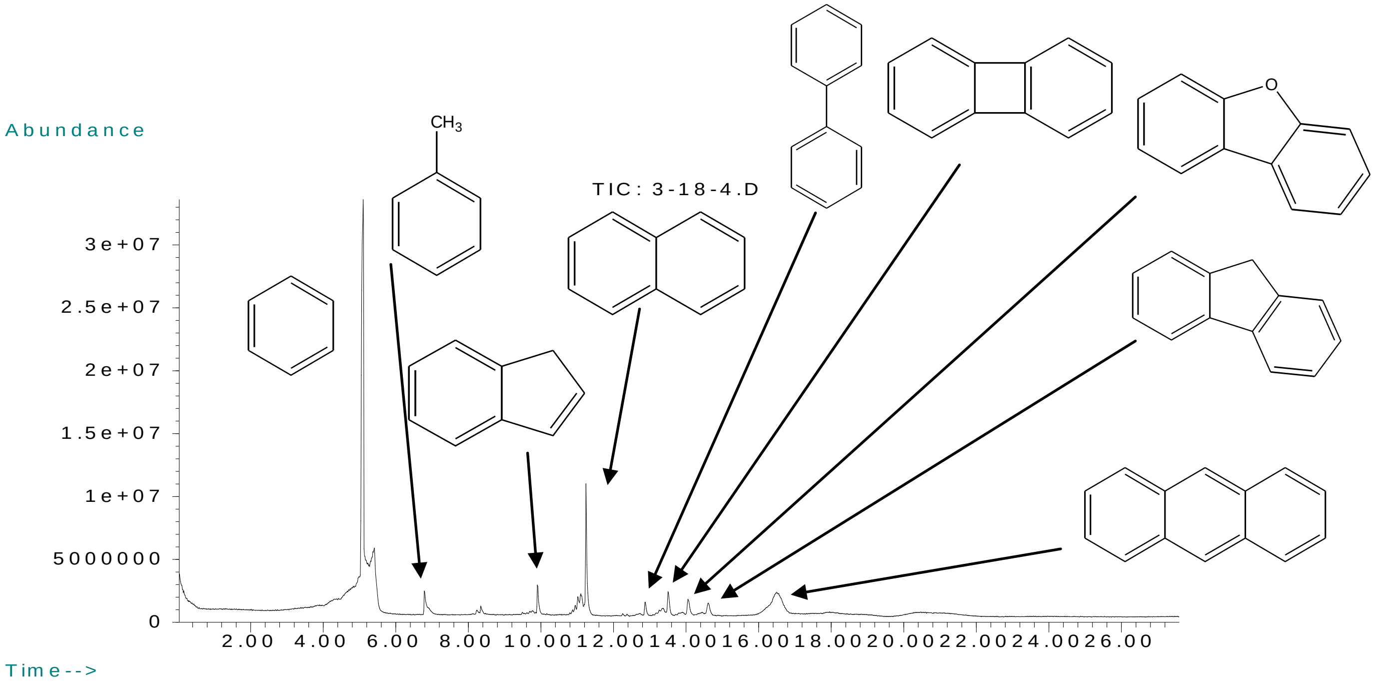


Figure B16. Total Ion Chromatogram (TIC) of Non-flame Retardant Sample under 21% O2 Condition at 900°C

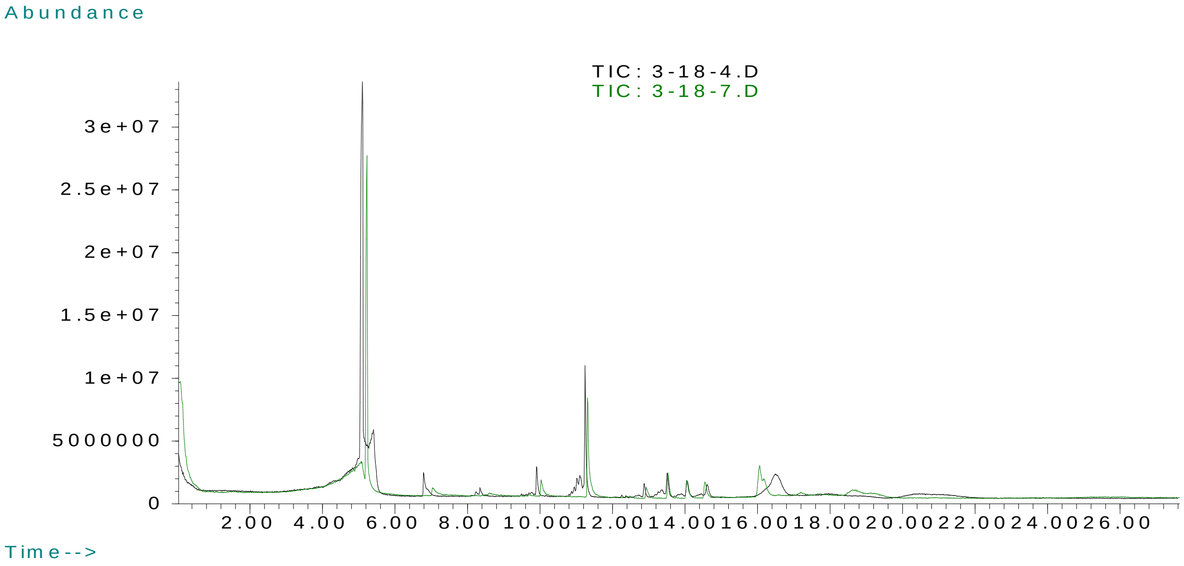


Figure B17. Overlaid TIC for Repeated Experiment (Non-flame Retardant Sample under 21% O2 Condition at 900°C)

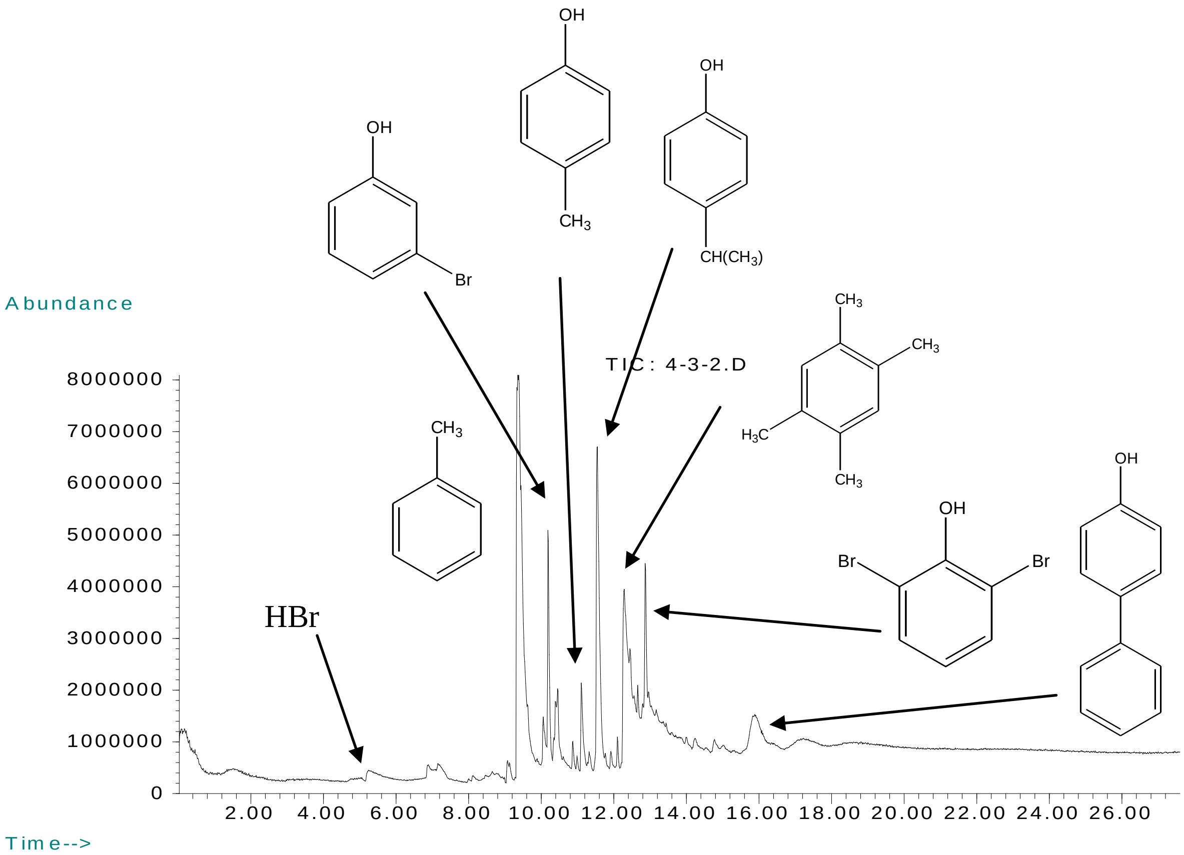


Figure B18. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 21% O2 Condition at 300°C

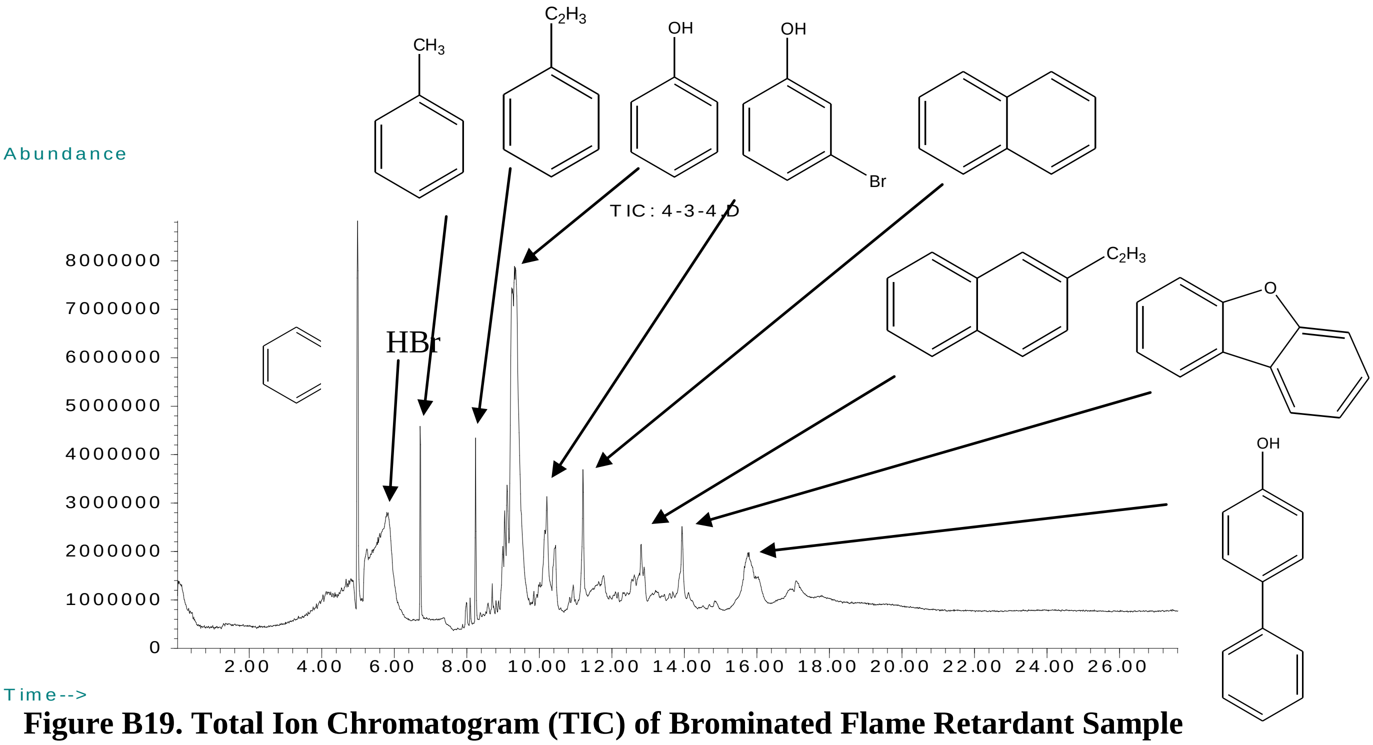


Figure B19. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 10% O2 Condition at 700°C

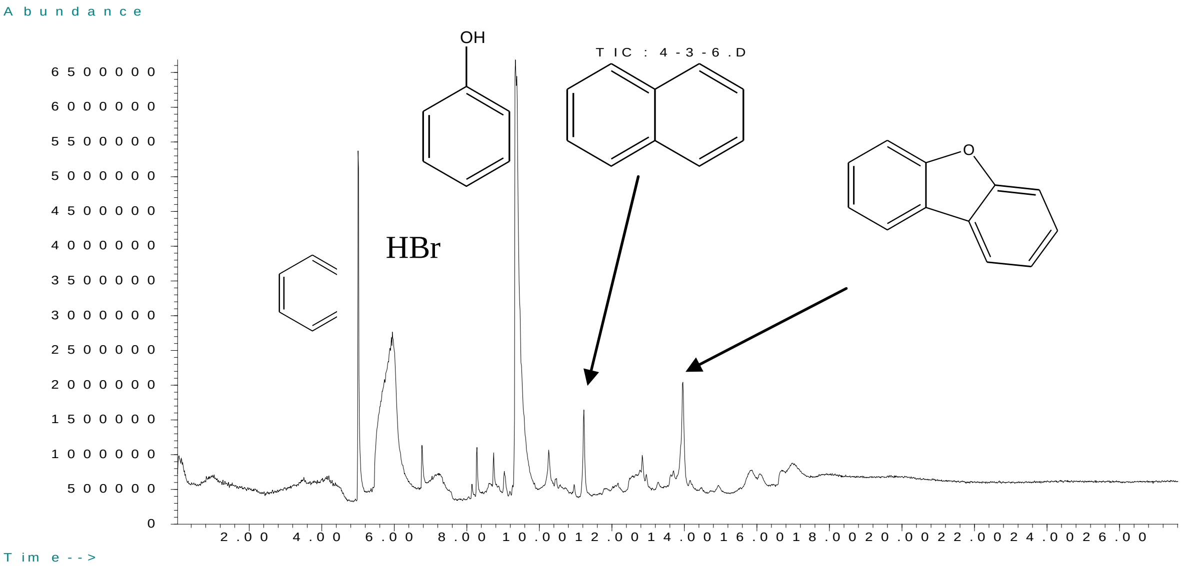


Figure B20. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 21% O2 Condition at 700°C

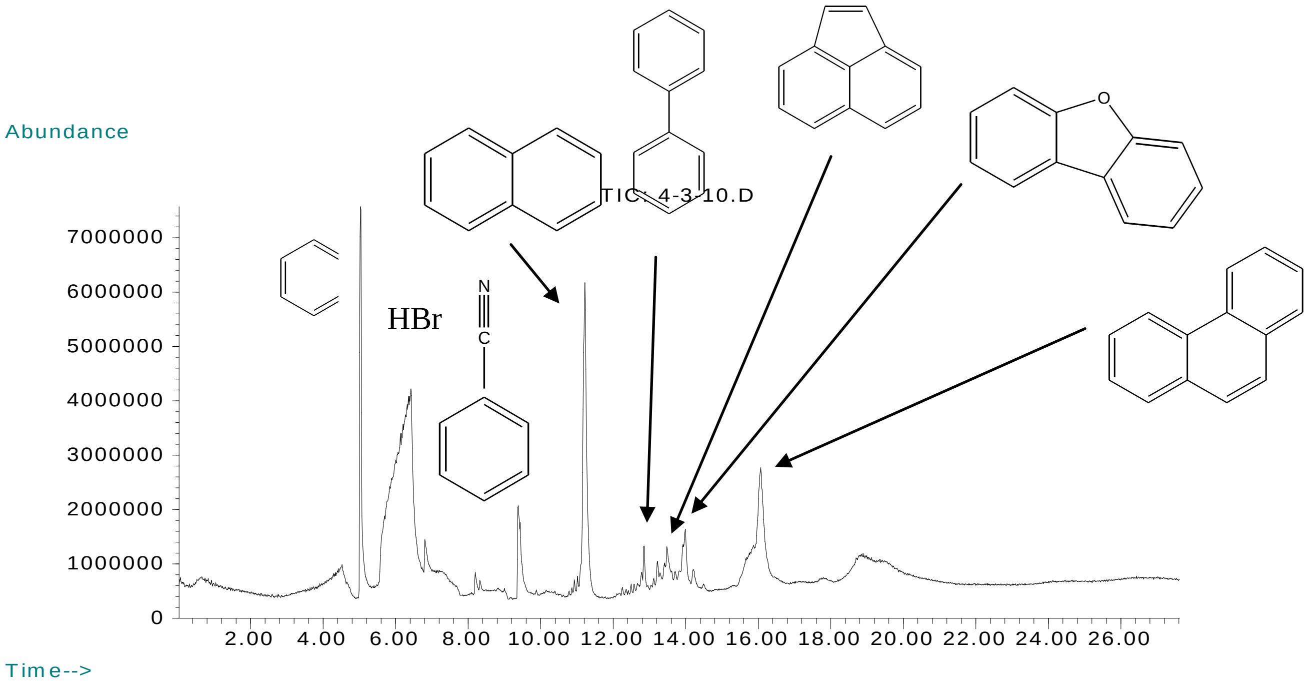


Figure B21. Total Ion Chromatogram (TIC) of Brominated Flame Retardant Sample under 21% O2 Condition at 900°C

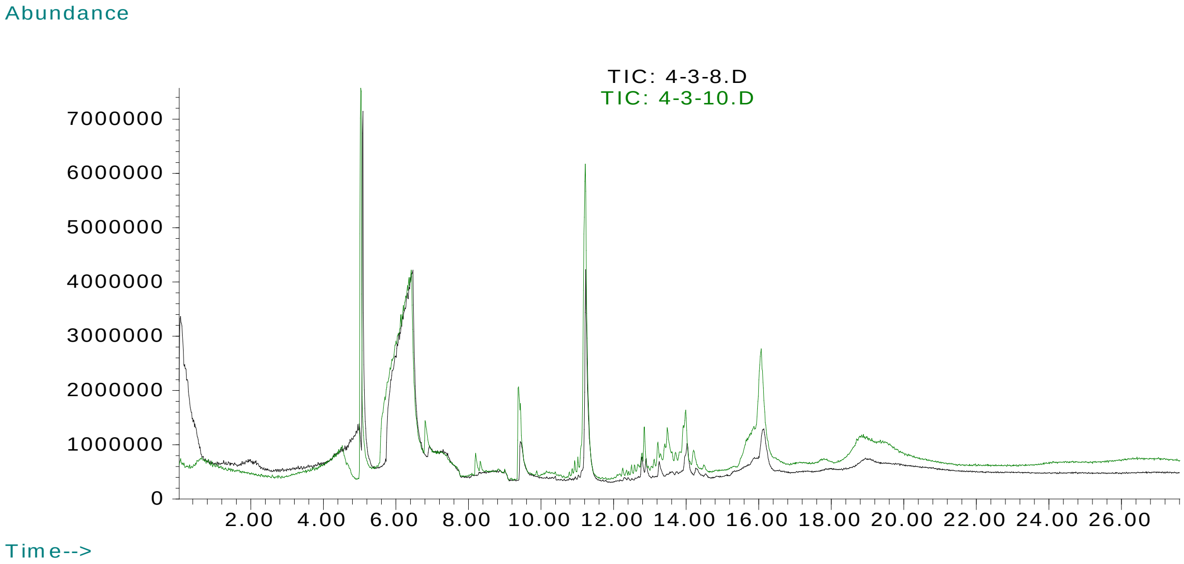


Figure B22. Overlaid TIC for Repeated Experiment (Brominated Flame Retardant Sample under 21% O2 Condition at 900°C)

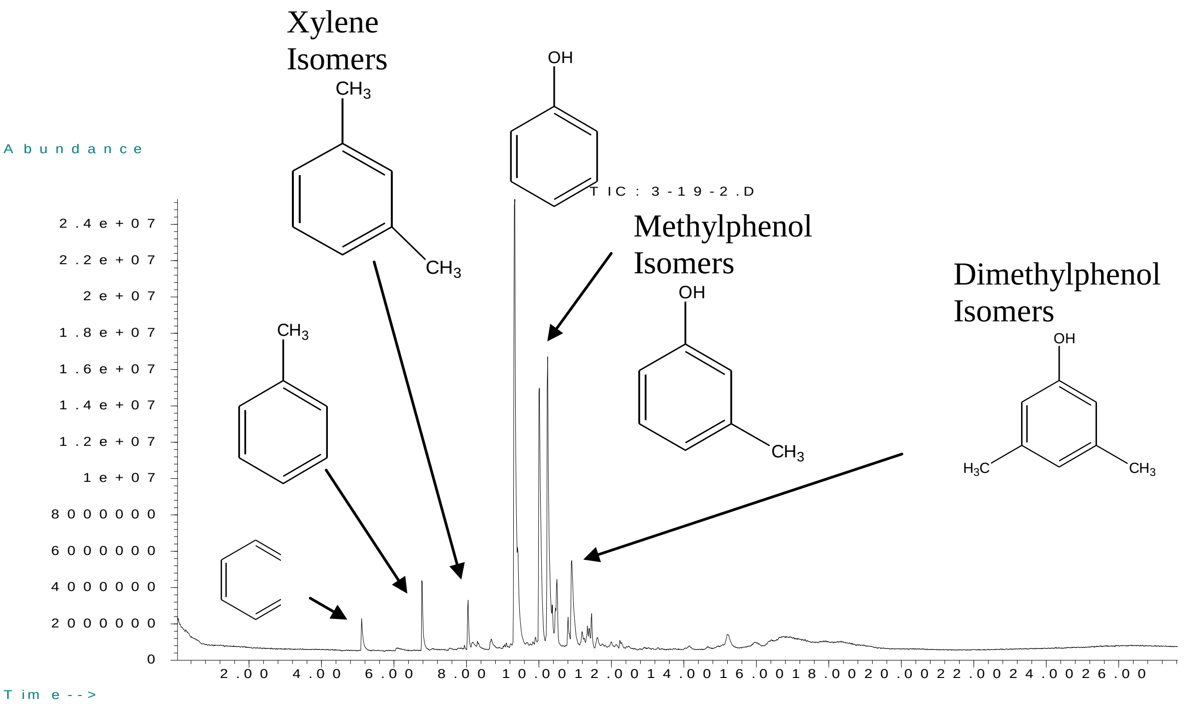


Figure B23. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 21% O2 Condition at 300°C

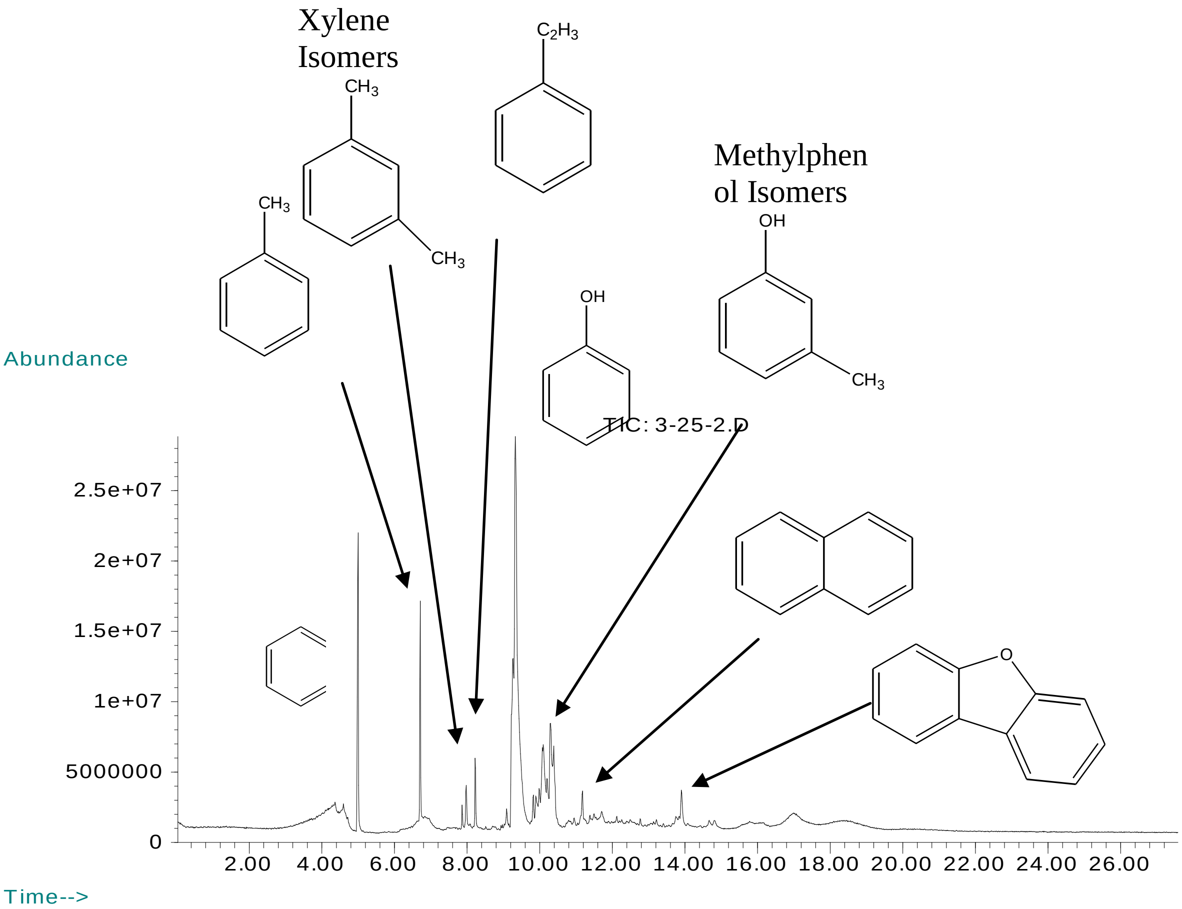


Figure B24. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 10% O2 Condition at 700°C

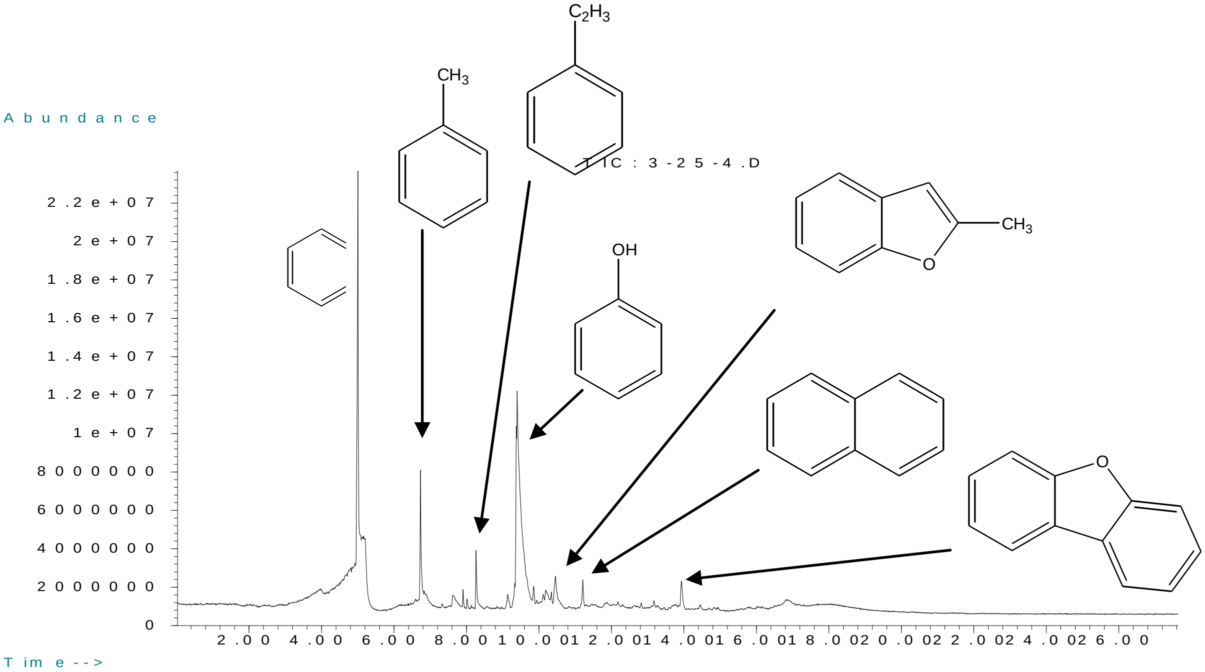


Figure B25. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 21% O2 Condition at 700°C

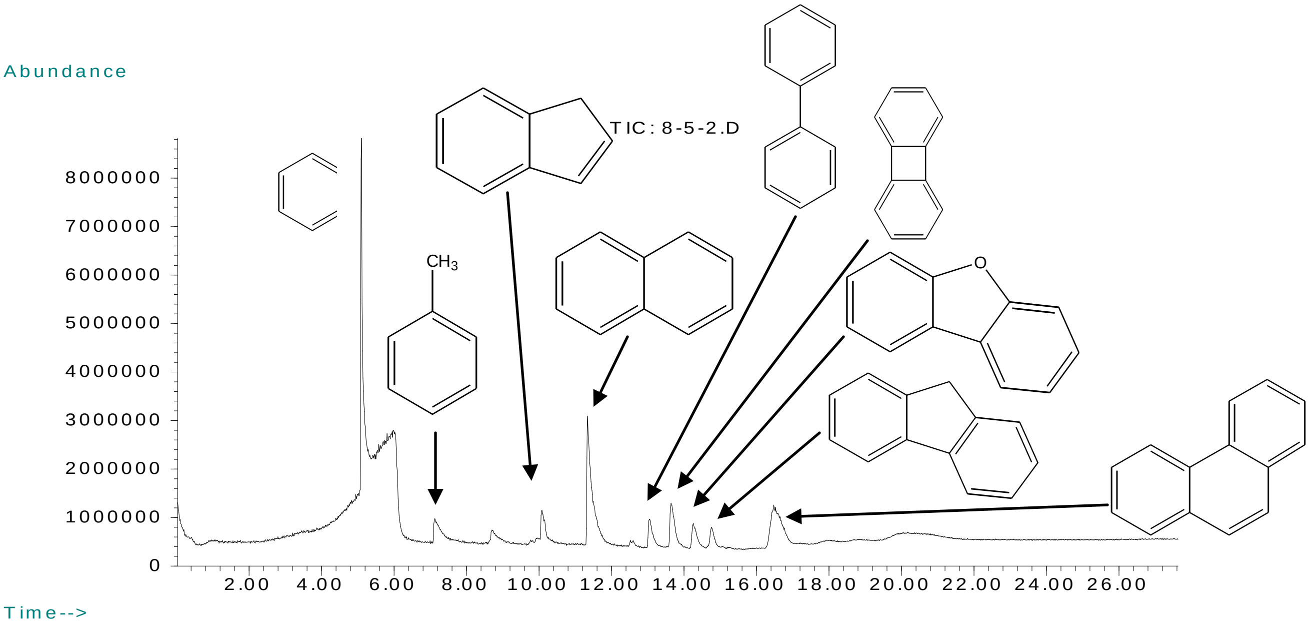


Figure B26. Total Ion Chromatogram (TIC) of Phosphorous Flame Retardant Sample under 21% O2 Condition at 900°C

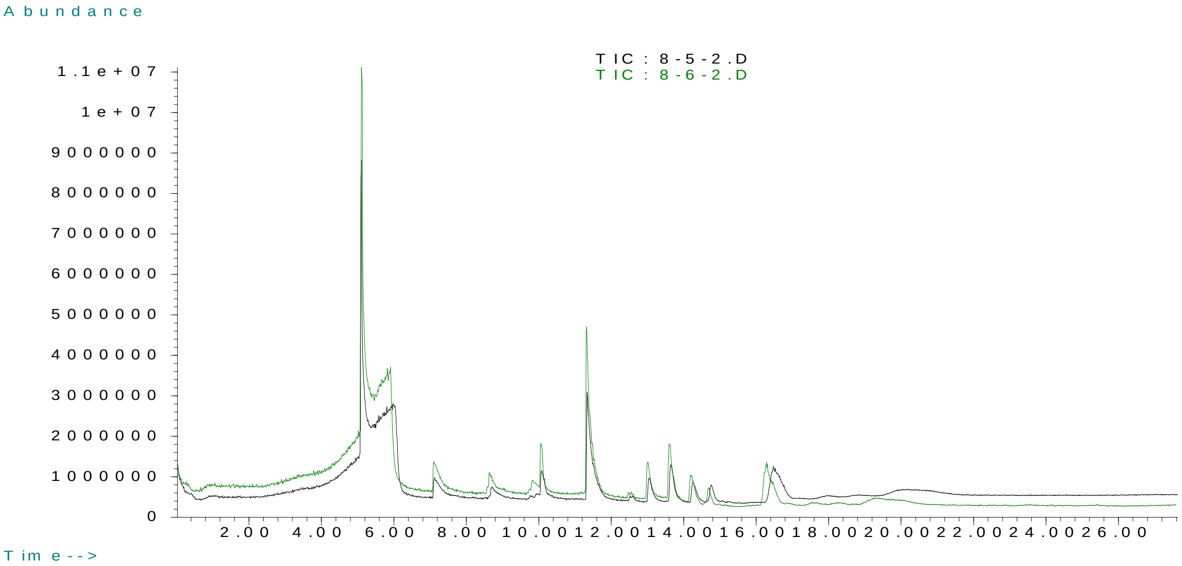


Figure B27. Overlaid TIC for Repeated Experiment (Phosphorous Flame Retardant Sample under 21% O2 Condition at 900°C)

Appendix C
Aqueous Sample Ion Chromatogram Analysis

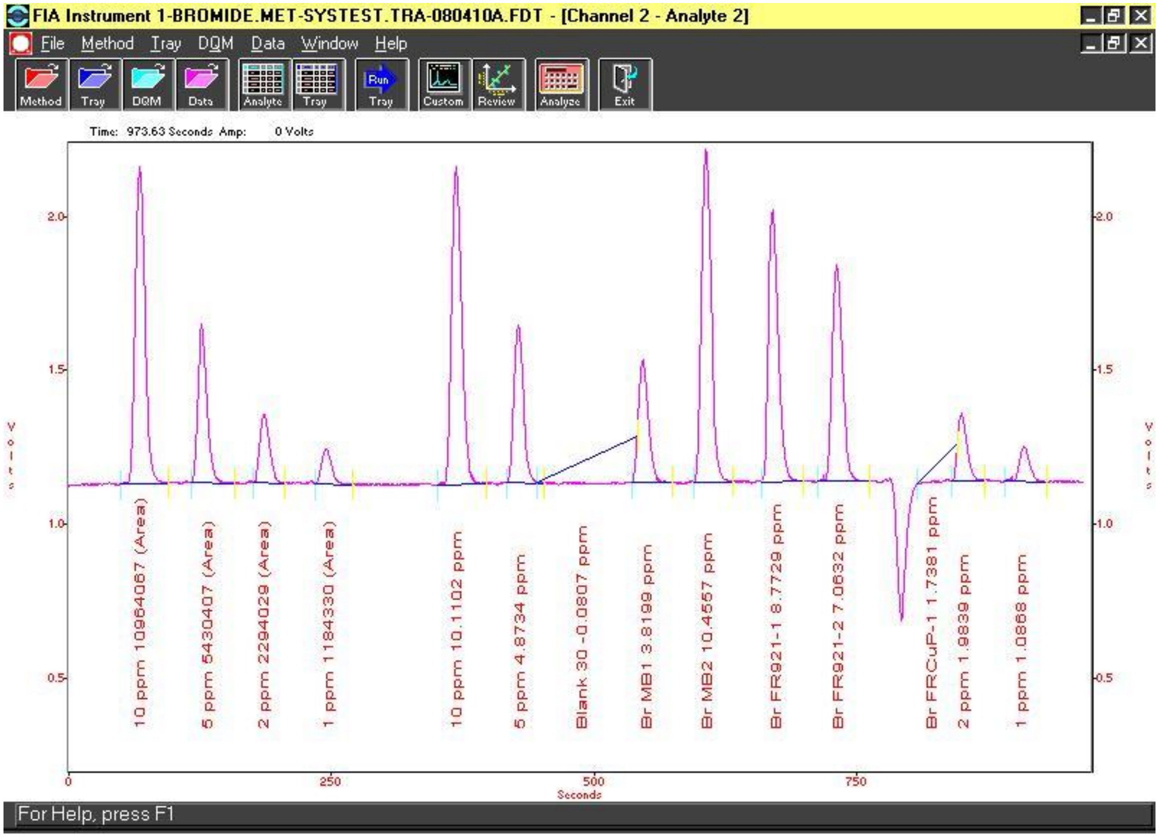


Figure C1. FIA Analysis of Aqueous Samples Run 1

Blank 30:	Blank Sample
BrMB1:	Aqueous sample for TBBA standard used for Br mass balance test.
BrMB2:	Bromide standard for cross check
BrFR921-1:	Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2.
BrFR921-2:	Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2, repeated.
BrFRCuP1:	Aqueous sample for Br flame retardant with Cu laminate combustion test at 900ºC in pyrolysis.

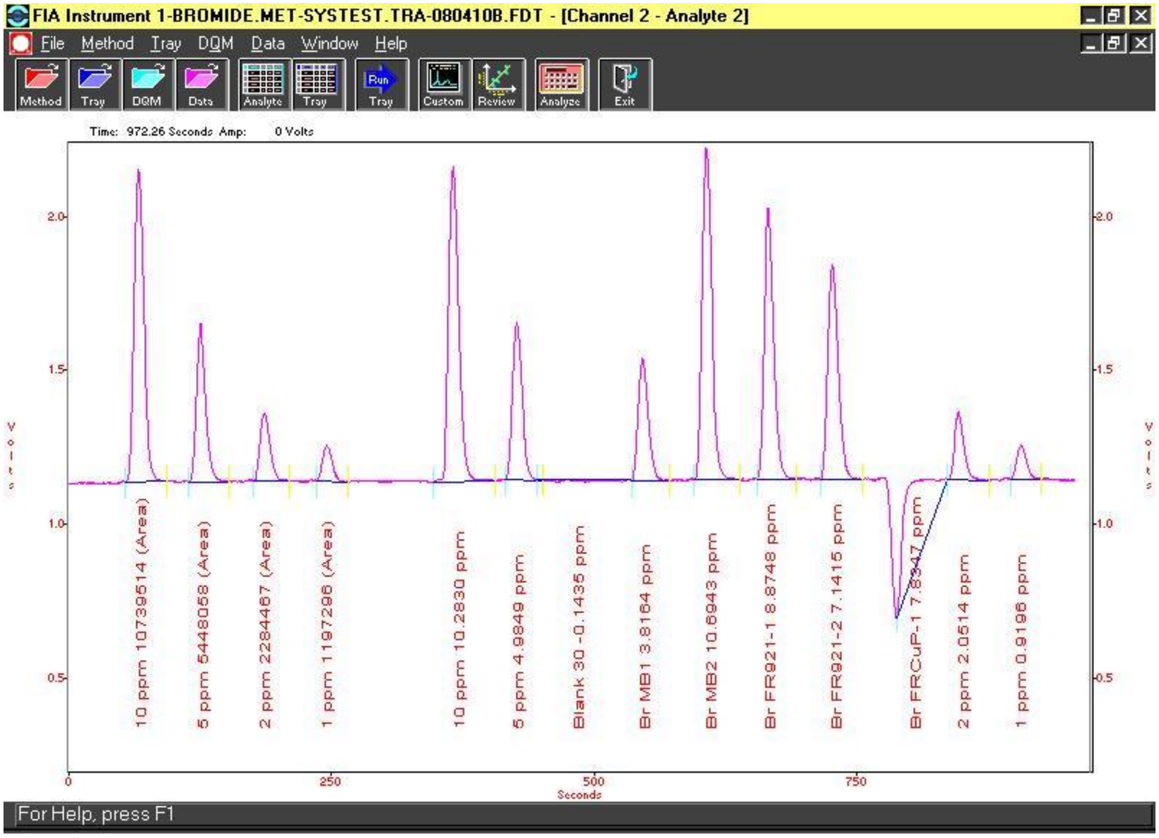


Figure C2. FIA Analysis of Aqueous Samples Run 2

Blank 30:	Blank Sample
BrMB1:	Aqueous sample for TBBA standard used for Br mass balance test.
BrMB2:	Bromide standard for cross check
BrFR921-1:	Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2.
BrFR921-2:	Aqueous sample for Br flame retardant combustion test at 900ºC with 21% O2, repeated.
BrFRCuP1:	Aqueous sample for Br flame retardant with Cu laminate combustion test at 900ºC in pyrolysis.

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX B

Sidhu, Sukh; Morgan, Alexander; Kahandawala, Moshan; Chauvin, Anne; Gullett, Brian; Tabor, Dennis. Use of Cone Calorimeter to Estimate PCDD/Fs and PBDD/Fs Emissions From Combustion of Circuit Board Laminates. U.S. EPA and UDRI. March 23, 2009

USE OF CONE CALORIMETER TO ESTIMATE PCDD/Fs AND PBDD/Fs EMISSIONS FROM COMBUSTION OF CIRCUIT BOARD LAMINATES

Sukh Sidhu, Alexander Morgan, Moshan Kahandawala,

Anne Chauvin, Brian Gullett, Dennis Tabor

UDRI and EPA

March 23, 2009

The purpose of this study was to use a cone calorimeter to measure emissions from fully ventilated combustion of printed circuit board laminates. The cone calorimeter (FTT Dual Cone Calorimeter) was modified in order to allow for isokinetic sampling of the exhaust gas. USEPA method 23 was used to sample and analyze Polychlorinated Dibenzo-p-Dioxins and Furans (PCDD/Fs) and Polybrominated Dibenzo-p-Dioxins and Furans (PBDD/Fs) from combustion of circuit board laminates. The cone calorimeter experiments were conducted at the University of Dayton Research Institute (UDRI). The exhaust gas samples were extracted and analyzed at the EPA Research Triangle Park laboratory. This report presents and discusses experimental and analytical data from both institutions.

BrFR or BFR or BR FR = laminate containing brominated flame retardant

PFR = laminate containing phosphorous based flame retardant

NFR = laminate without a flame retardant

MATERIAL AND METHODS

Cone Calorimeter

The cone calorimeter is a fire testing instrument that measures the inherent flammability of a material through the use of oxygen consumption calorimetry [1]. It is based on the principle that the net heat of combustion of any organic material is directly related to the amount of oxygen required for combustion [2]. The cone calorimeter is a standard technique under ASTM E-1354/ISO 5660 [3, 4] and is commonly used as a fire safety engineering tool. Under the ASTM E-1354/ISO 5660 method, small samples (100 cm^2 squares up to 50-mm thick) of combustible materials are burned and a wide range of data can be obtained. Through oxygen consumption calorimetry, heat release rate data can be obtained and sensors on the cone calorimeter can measure smoke release, CO/CO_2 production rates, mass loss rate and several other flammability properties such as time to ignition and fire growth rate.

A schematic of the UDRI cone calorimeter apparatus is shown in Figure 1. At the core of the equipment is a radiant cone heater, hence the name ‘cone calorimeter’. A sample is placed at the center of the cone heater on the sample holder with dimensions of 100 mm x 100 mm. The cone heater provides a constant heat flux to the sample. Ignition of the sample is provided by a spark igniter located above the sample. The exhaust gas contains smoke and products of combustion. The constant ventilation is maintained by the blower. The cone calorimeter mimics a well-ventilated forced combustion of an object being exposed to a constant heat source and constant ventilation [5, 6].

Several measurements can be obtained from the cone calorimeter. A load cell continuously measures the mass loss of the sample as it burns. Gases from the fire are carried past a laser photometer beam to measure smoke density and to a sampling ring which carries the gases to a combined $CO/CO_2/O_2$ detector. Once the gases from the sampling ring have been analyzed, one can obtain CO and CO_2 production rates as a function of time which can give insight into the heats of combustion for the material, as well as combustion efficiency. Oxygen consumption is measured in the exhaust stream using an oxygen sensor (paramagnetic). The heat release rate is determined from oxygen consumption calorimetry. Temperature and pressure measurements are also taken at various locations in the exhaust duct.

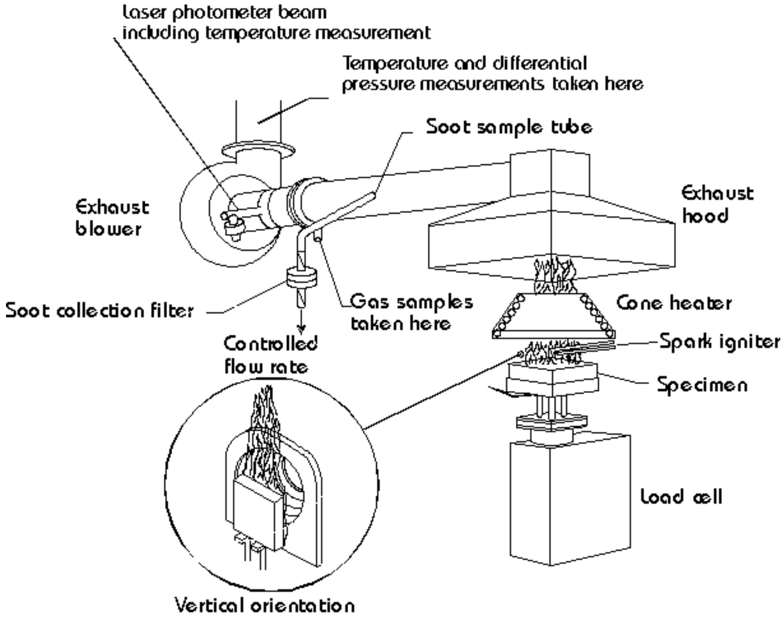


Figure 1. Schematic of Cone Calorimeter used at UDRI

The Cone calorimeter data collected during a test can reveal scientific information about material flammability performance. All measured data are defined below:

- Time to ignition (Tig): Measured in seconds, this is the time to sustained ignition of the sample. Interpretation of this measurement assumes that shorter times to ignition mean that samples are easier to ignite under a particular heat flux.
- Heat Release Rate (HRR): The rate of heat release, in units of kW/m^2, as measured by oxygen consumption calorimetry.
- Peak Heat Release Rate (Peak HRR): The maximum value of the heat release rate during the combustion of the sample. The higher the peak HRR, the more likely that flame will self-propagate on the sample in the absence of an external flame or ignition source. Also, the higher the peak HRR, the more likely that the burning object can cause nearby objects to ignite.
- Time to Peak HRR: The time to maximum heat release rate. This value roughly correlates the time it takes for a material to reach its peak heat output, which would in turn sustain flame propagation or lead to additional flame spread. Delays in time to peak HRR are inferred to mean that flame spread will be slower in that particular sample, and earlier time to peak HRR is inferred to mean that the flame spread will be rapid across the sample surface once it has ignited.
- Time to Peak HRR – Time to Ignition (Time to Peak HRR – Tig): This is the time in seconds that it takes for the peak HRR to occur after ignition rather than at the start of the test (the previous measurement). This can be meaningful in understanding how fast the sample reaches its maximum energy release after ignition, which can suggest how fast the fire grows if the sample itself catches fire.

- Average Heat Release Rate (Avg HRR): The average value of heat release rate over the entire heat release rate curve for the material during combustion of the sample.
- Starting Mass, Total Mass Lost, Weight % Lost. These measurements are taken from the load cell of the cone calorimeter at the beginning and end of the experiment to see how much total material from the sample was pyrolyzed/burned away during the experiment.
- Total Heat Release (THR). This is measured in units of MJ/m^2 and is basically the area under the heat release rate curve, representing the total heat released from the sample during burning. The higher the THR, the higher the energy content of the tested sample. THR can be correlated roughly to the fuel load of a material in a fire, and is often affected by the chemical structure of the material.
- Total Smoke Release: This is the total amount of smoke generated by the sample during burning in the cone calorimeter. The higher the value, the more smoke generated either due to incomplete combustion of the sample, or due to the chemical structure of the material.
- Maximum Average Heat Rate Emission (MAHRE): This is a fire safety engineering parameter, and is the maximum value of the average heat rate emission, which is defined as the cumulative heat release (THR) from t=0 to time t divided by time t [7]. The MAHRE can best be thought of as an ignition modified rate of heat emission parameter, which can be useful to rank materials in terms of ability to support flame spread to other objects.
- Fire Growth Rate (FIGRA): This is another fire safety engineering parameter, determined by dividing the peak HRR by the time to peak HRR, giving units of kW/m^2 per second. The FIGRA represents the rate of fire growth for a material once exposed to heat, and higher FIGRA suggest faster flame spread and possible ignition of nearby objects [1].

Isokinetic Sampling

In this project, the cone calorimeter was utilized to combust the various circuit board laminates and collect products released during their combustion. The USEPA method 23 was used to isokinetically sample a portion of the exhaust gases flowing through the exhaust duct. The cone calorimeter was modified to allow for the isokinetic sampling device to be inserted into the exhaust duct.

The main characteristic of isokinetic sampling is that the extraction of the gas sample from the main gas stream is at the same velocity as the gas travelling through the stack. This sampling method is easily adaptable and is commonly used to test for many organic pollutants such as polychlorinated biphenyls (PCBs), dioxins/furans and polycyclic aromatic hydrocarbons (PAHs) [8]. The compounds of interest are retained in a glass fiber filter and Amberlite XAD-2 adsorbent resin.

Apex Instruments Model MC-500 Series Source Sampler Console and Isokinetic System were used for this experiment and contained five main components: the source sampler console, the external vacuum pump unit, the probe assembly, the modular sample case and the umbilical cables. A picture of the Apex instrument isokinetic source sampling equipment is shown in Figure 2.

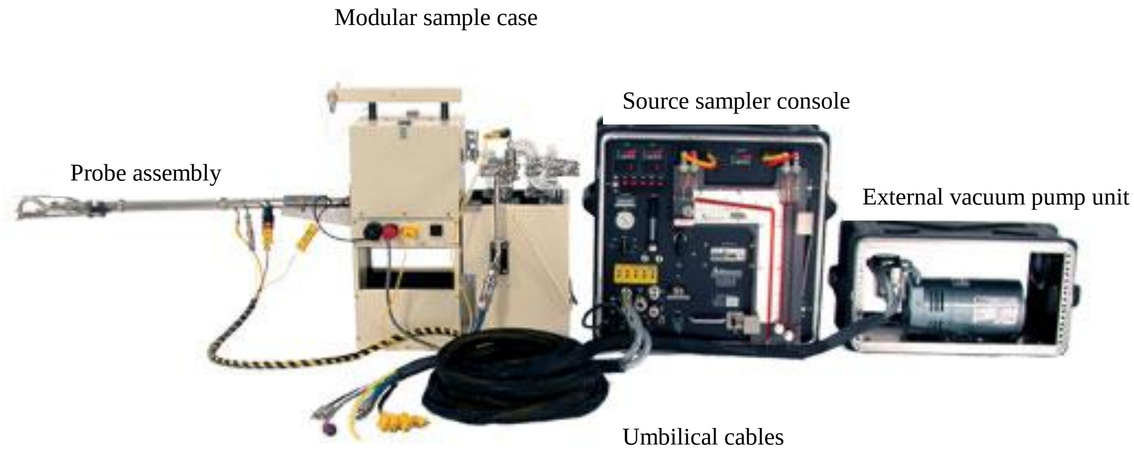


Figure 2. Isokinetic Sampling train used at UDRI

The modular sample case contained a heated box for the filter assembly and a cold box for the impinger glassware and condenser. The sampling nozzle of the heated transfer line was inserted into the exhaust duct, which was modified by adding holes into the side to allow for the device to be inserted. Figure 3 shows the modifications made to the exhaust system of the cone calorimeter. A picture of the cone calorimeter and the isokinetic sampling system assembly is shown in Figure 4.

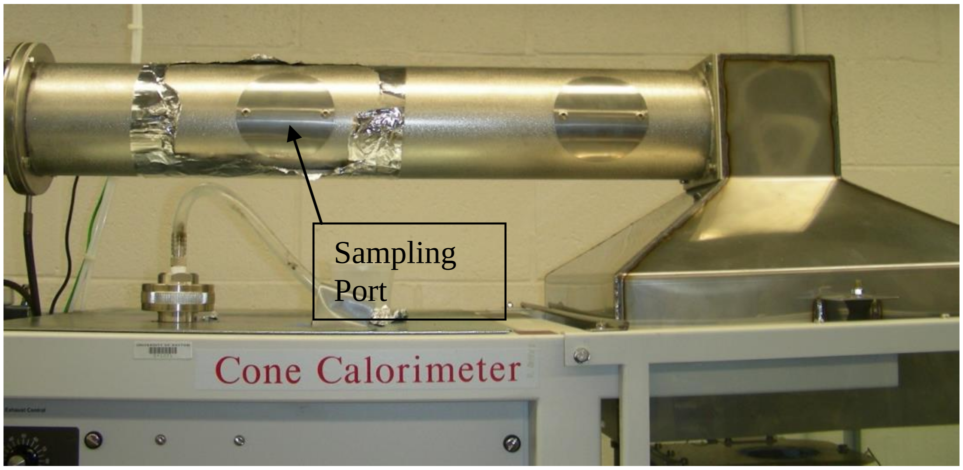


Figure 3. Modification of duct and sampling port of the UDRI cone calorimeter

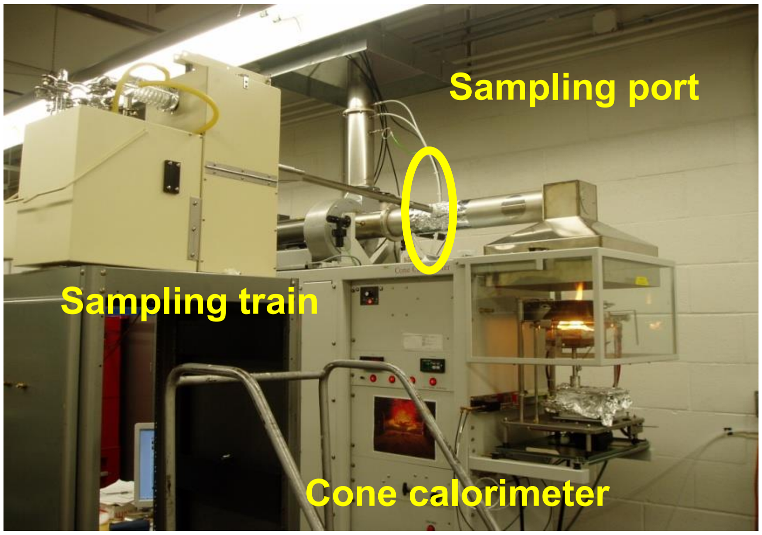


Figure 4. Cone calorimeter and isokinetic sampling system assembly

The heated probe connected the nozzle to the filter assembly where the soot was retained. The mass of the filter before and after sampling was recorded to obtain the mass of soot formed during the combustion of the samples (see data in the Appendix, Table 1). The filter assembly was also connected to a condenser followed by an adsorbent trap and a series of four impingers. The moisture formed in the condenser deposited as droplets in the first empty impinger and therefore could not be quantified. The adsorbent trap contained about 40 g of hydrophobic resin XAD-2, glass wool and 100 µL of surrogate standard solution. The surrogate standard solution contained ${}^{13}C_{12}$ labeled standards of PCDD/Fs to evaluate the method. Due to lack of standards for PBDD/Fs, no ${}^{13}C_{12}$ labeled standards of PBDD/Fs were spiked into the samples prior to sampling. XAD-2 was used to absorb the soluble organic compounds from the effluent gas. The second impinger contained about 100 mL of water, the third one was empty and the fourth one contained about 200 g of silica gel and was connected to a thermocouple. All three impingers were used to collect any extra moisture in the effluent gas. The mass of silica gel was recorded before and after sampling to obtain the mass of moisture content in the effluent gas (see data in Appendix, Table 1). The third impinger appeared to stay dry throughout the experiment (few water droplets on the sides could not be quantified). The amount of water in the second impinger was recorded before and after sampling (see data in Appendix, Table 1) and appeared to decrease. This might be explained by the fact that some of the water could have been carried away by the effluent gas and was collected in the fourth impinger with the silica gel.

After assembling the sampling train, the system had to be checked for leaks. Throughout the runs, the temperature inside the probe and inside the filter was controlled and maintained at 120°C from the source sampler console. The cold box temperature was maintained under 20°C by adding ice water to it. The pump flow rate was maintained at 0.1104 L/s and the exhaust flow rate was maintained at 15 L/s throughout the experiment. The flow rate through the probe was controlled and maintained steady by adjusting the flow rate through the stack and therefore a pitot tube was not necessary.

After sampling, the filter and soot, as well as the soot in the probe, nozzle and front half of the filter holder, XAD-2 resin and water from the second impinger were combined for a single analysis. The filter was placed in container No.1. Container No. 2 contained the soot deposited in the nozzle, transfer probe and front half of filter holder as well as all the methylene chloride and acetone rinses. Container No. 3 contained the same material as container No. 2 with toluene as the rinse solvent. The water was also placed in a container for analysis and the silica gel was discarded. After sampling, the duct and exhaust hood were dismantled and thoroughly cleaned with hexane to avoid any risk of contamination from combustion of one type of circuit board to the next. The sampling method and sample recovery followed the USEPA method 23 for the determination of emissions of PCDD’s and PCDF’s from stationary sources (9). A schematic of the isokinetic sampling train is shown in Figure 5.

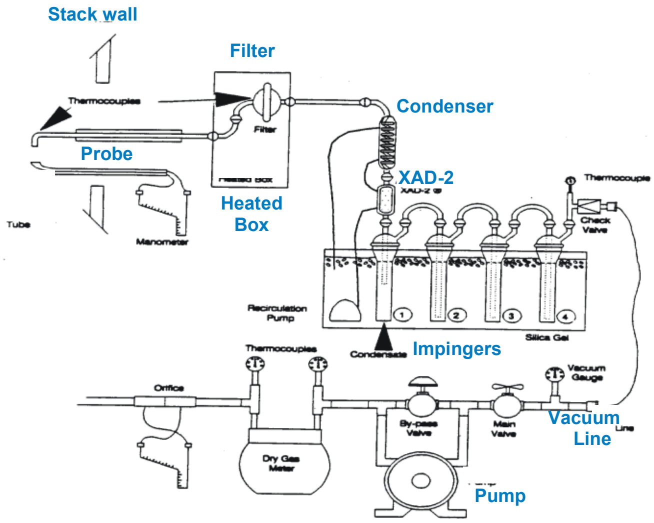


Figure 5. Schematic of isokinetic sampling train

For the first set of experiments (combustion of BrFR laminate), the temperature inside the stack dropped below 100°C before it even reached the sampling probe. The temperatures below 100°C can lead to condensation inside the stack; therefore, to prevent condensation inside the stack and ensure proper transport of gaseous organic compounds formed, a heating tape was wrapped around the stack to maintain the temperature inside the stack between 100°C and 130°C during combustion. In order to monitor the temperature inside the stack during combustion of the samples, a thermocouple was placed on the inside wall of the stack right behind the nozzle. Two other thermocouples were added to the outside wall. Please see Appendix, Table 3 for inside wall temperature data. Note that for the first set of experiments (BrFR) the cone calorimeter did not have the heating tape and thermocouples. However, a repeat run was made for the BrFR laminate which included the heating tape around the stack and thermocouples.

Samples tested

Three types of circuit board samples were provided: laminates containing brominated flame retardant, non-halogen flame retardant (Phosphorous- based) and no-flame retardant. The laminates were very thin (~0.4mm thick) and contained copper strips. They were made of a mixture of epoxy resin and e-glass [1]. The three types of circuit board are summarized in Table 1.

Table 1. Circuit Board Types

Circuit Board types	Description	Picture
BrFR	Circuit board containing Brominated Flame Retardant	
NFR	Circuit board without Flame Retardant	
PFR	Circuit Board containing Phosphorous Flame Retardant	

Preparation of Samples

Since the laminates provided were too large to be tested as is in the cone calorimeter, the samples were cut into roughly 100 cm^2 square pieces for cone calorimeter testing. Samples were not conditioned in any way prior to testing. Depending upon how the original laminates were cut, the samples had 1 or 2 copper strips as shown in Figure 6.

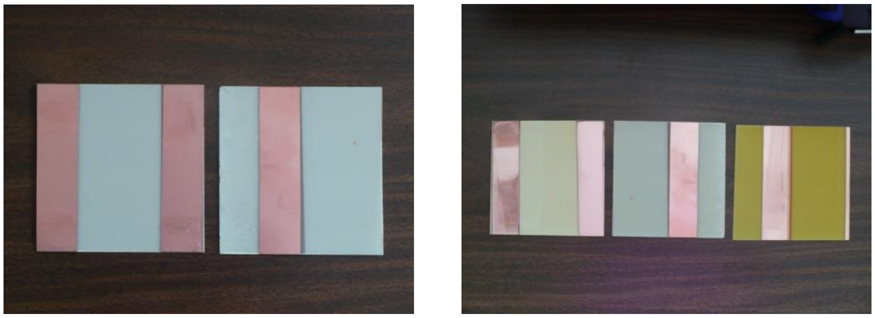


Figure 6. Two-strip and one-strip circuit boards

Initially, it was estimated that 6 thin laminates had to be stacked and burned together in order to reach a temperature inside the duct of about 120°C during combustion (120°C is the USEPA method 23 recommended transfer line temperature); this was also the maximum number of laminates per stack for which the exhaust gas flow rate was sufficient to remove the smoke produced during combustion (if the number of laminates per stack was increased, smoke came into the lab). The laminate pieces were selected and configured in six layer stacks where 2 x two-strip laminates and 4 x one-strip laminates where stacked together. The stacking sequence ensured that each test sample had the same amount of copper metal in similar configuration. One single one-strip laminate as well as one single two-strip laminate were also burned separately to determine the effect of copper on burning patterns and smoke emissions. Each sample was wrapped in aluminum foil such that only the upper side was exposed to the constant heat flux. The aluminum foil helped to keep the samples together as they burned (preventing them from falling from the sample holder) and directed the smoke and flames toward the exhaust hood. Figure 7 shows a sample wrapped in aluminum foil.

Figure 7. Sample wrapped in aluminum foil

Five runs were conducted in series for each circuit board type where the first three runs consisted of 6- layer samples and the last two runs consisted of 1 one-strip laminate and 1 two-strip laminate sample. The combustion products for all five runs were collected for a single analysis for a given type of circuit board. The initial mass of each sample wrapped in aluminum foil was recorded for each run and is summarized in Table 2. Table 2 also summarizes the sequence in which the samples were burned.

Table 2. Description of Samples

Circuit Board Type	Date sampled	Run	Number of laminates	Description (one or two-strip laminate)	Sample ID
BrFR	06/05/08	1	6	2 two-strip and 4 one-strip	Br FR Epoxy Laminate, 6 plies, run 1
		2	6	2 two-strip and 4 one-strip	Br FR Epoxy Laminate, 6 plies, run 2
		3	6	2 two-strip and 4 one-strip	Br FR Epoxy Laminate, 6 plies, run 3
		4	1	one-strip	Br FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4
		5	1	two-strip	Br FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5
NFR	06/16/08	1	6	2 two-strip and 4 one-strip	No FR Epoxy Laminate, 6 plies, run 1
		2	6	2 two-strip and 4 one-strip	No FR Epoxy Laminate, 6 plies, run 2
		3	6	2 two-strip and 4 one-strip	No FR Epoxy Laminate, 6 plies, run 3
		4	1	one-strip	No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4
		5	1	two-strip	No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5
PFR	06/17/08	1	6	2 two-strip and 4 one-strip	Non Hal FR Epoxy Laminate, 6 plies, run 1
		2	6	2 two-strip and 4 one-strip	Non Hal FR Epoxy Laminate, 6 plies, run 2
		3	6	2 two-strip and 4 one-strip	Non Hal FR Epoxy Laminate, 6 plies, run 3
		4	1	two-strip	Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4
		5	1	one-strip	Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5
(Repeat BrFR)	06/18/08	1	6	2 two-strip and 4 one-strip	Br FR Repeat run 1
		2	6	2 two-strip and 4 one-strip	Br FR Repeat run 2
		3	6	2 two-strip and 4 one-strip	Br FR Repeat run 3
		4	1	one-strip	Br FR Repeat run 4
		5	1	two-strip	Br FR Repeat run 5

Sampling

The cone calorimeter experiments were conducted on a FTT Dual Cone Calorimeter following the ASTM E-1354-04 method at one heat flux (50 kW/m^2), but some modifications were made to the method: the isokinetic sampling system was added to sample the exhaust gas and the heating tape was wrapped around the duct for the NFR, PFR, BrFR and BrFR (repeat) samples. A constant heat flux of 50 kW/m^2 was maintained by setting the cone temperature at about 759°C. Samples were tested in triplicate without frame and grid, with the back side of each sample wrapped in aluminum foil and an exhaust flow was maintained at 15 L/s. All samples were tested copper side up [3]. The initial and final ambient conditions during the combustion of samples were recorded and are summarized in Table 3.

Table 3. Ambient conditions during experiment

	BrFR		NFR		PFR		BrFR (repeat)	
	Initial	Final	Initial	Final	Initial	Final	Initial	Final
Temperature (°C)	26.5	27.5	26.5	NA	24	28	24	24
Humidity (%)	46	45	33	32	35	29	35	34
Pressure (mbar)	1088	1088	1084	1084	1091	1089	1087	1086

Each sample was ignited and allowed to burn until the flames disappeared. For the 6-layer Non Hal FR Laminate run 2 and 3, and Br FR Laminate repeat run 3, the flame had to be re-ignited shortly after initial ignition. The burning times for each sample as well as the initial mass, mass burnt and volumes of gas sampled were recorded and are summarized in Table 4.

Table 4. Data taken during Combustion of Samples

Sample ID	Starting mass (g)	Mass lost (g)	Total sampling time (s)	Volume sampled (ft3)	Comments
Br FR Epoxy Laminate, 6 plies, run 1	61.8	19.2	426	10.1	No heating tape around cone calorimeter duct
Br FR Epoxy Laminate, 6 plies, run 2	62.2	18.5	400		
Br FR Epoxy Laminate, 6 plies, run 3	60.4	17.6	374		
Br FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	11.9	2.5	99		
Br FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	10.2	2.8	89		
No FR Epoxy Laminate, 6 plies, run 1	61.5	16.6	512	12.4	Heating tape
No FR Epoxy Laminate, 6 plies, run 2	64.5	15.9	622		
No FR Epoxy Laminate, 6 plies, run 3	63.8	17.6	534		
No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	12.6	3.4	129		
No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	11.0	3.5	110		
Non Hal FR Epoxy Laminate, 6 plies, run 1	63.3	14.3	670	13.9	Heating tape; Run 2 and 3 were re-ignited after 4 min
Non Hal FR Epoxy Laminate, 6 plies, run 2	64.3	14.9	668		
Non Hal FR Epoxy Laminate, 6 plies, run 3	64.5	13.8	652		
Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4	12.6	2.2	179		
Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5	11.0	2.8	145		
Br FR Repeat run 1	61.64	19.1	360	10.5	Heating tape; Run 3 was re-ignited after 1 min
Br FR Repeat run 2	60.03	18.5	300		
Br FR Repeat run 3	61.25	18.7	300		
Br FR Repeat run 4	10.65	1.3	60		
Br FR Repeat run 5	12.15	3.4	60		

All conditions during the combustion of the samples and collection of organic compounds are summarized in Table 5.

Table 5. Summary of Conditions during Combustion of Samples

Parameters	Conditions
Heat Flux (kW/m^2)	50
Stack Gas Flow Rate (L/s)	15
Sampling Flow Rate (L/s)	0.1104
Pump Flow Rate (L/s)	0.1104
Probe Temperature (°C)	120
Filter Temperature (°C)	120
Cold Box Temperature (°C)	<20
Cone Temperature (°C)	759

Extraction and Analysis

After sampling, Container No. 1 (filter), Container No. 2 (soot deposited in the nozzle, transfer probe and front half of filter holder as well as all the methylene chloride and acetone rinses), Container No. 3 (same material as container No. 2 with toluene as the rinse solvent), and an another container containing the XAD-2 and glass wool were sealed and recorded on a chain of custody form. All containers were sent to the EPA Research Triangle Park laboratory for extraction and analysis.

The EPA Research Triangle Park laboratory received the samples from UDRI and confirmed them against the chain of custody form. The samples had been spiked at UDRI with PCDD/F pre-sampling spikes to confirm the sampling process. The samples were spiked again just before extraction with PBDD/F surrogates and internal standards for both the PCDD/F and

PBDD/F. The samples were then extracted with methylene chloride for 3.5 hours and then with toluene overnight. The cooler methylene chloride extraction is used in low light conditions to extract the majority of the brominated compounds due to concerns that they could degrade due to light exposure, the higher extraction temperature of toluene, and longer extraction times. The toluene extraction procedure was used to ensure that the standard method of extraction (EPA Method 23 for Dioxin Analysis) was also completed. After extraction, the extracts were concentrated with a Snyder column and then filtered. The final volume was 1 milliliter. The extracts were very dark so only one quarter of the extract was used for further clean-up and analysis. Equal portions of the methylene chloride and toluene extracts were combined and diluted with hexane for the clean-up. The extracts were then processed through acidic, neutral, and basic silica gel, and then adsorbed onto basic alumina and washed with dilute methylene chloride in hexane. The target compounds were then transferred to carbon/celite with 50/50 methylene chloride/hexane, washed with benzene/ethyl acetate and then eluted from the carbon celite with toluene. The final fraction was concentrated to 100 microliter and analyzed with high resolution gas chromatography/high resolution mass spectrometry [10].

The samples were analyzed using an isotope dilution method where isotopically labeled internal standards and surrogate standards were incorporated prior to sampling and extraction. The surrogate standards were spiked prior to sampling and their recoveries gave a measure of the sampling process efficiency. The internal standards were spiked prior to extraction and allowed quantifying the PCDD/Fs and PBDD/Fs present in the samples. According to the USEPA method 23, recoveries of the pre-extraction standards must be between 40 and 130 percent for tetra- through hexachlorinated compounds and 25 to 130 percent for the hepta- and octachlorinated homologues. All recoveries for PCDD/Fs pre- sampling surrogate standards must be between 70 and 130 percent [9]. Percent recovery limits for PBDD/Fs are not available at the moment. Overall, it was found that PCDD/Fs pre-sampling and pre-extraction surrogate standard recoveries fell within the acceptable range (see Appendix 2 for recoveries data). Standard recoveries never fell below the lowest limit, but for the isotopes $13C^{12}$ 2,3,7,8 - TeCDF in the BrFR run and $13\ C^{12}$ 1,2,3,4,7,8,9 - HpCDF in the PFR run, the percent recovery was slightly above the highest limit, which means that there was a possibility of breakthrough in the sampling train.

A blank run sample was also analyzed for PCDD/Fs and PBDD/Fs analysis to demonstrate that no contamination was contributed by laboratory instruments (see Appendix 2 for data).

RESULTS AND DICUSSION

CO/CO_2 production/ O_2 consumption data

The gas sampled in the sampling ring was analyzed by a $CO/CO_2/O_2$ detector which allowed measurement of CO/CO_2 production rates and O_2 consumption rate as a function time. The total production rates and consumption rates per initial sample mass are presented in Table 6. Note that for the repeat run for BrFR samples, $CO/CO_2/O_2$ data is not provided because it is not affected by the temperature of exhaust duct.

Table 6. Total CO/CO_2 production rate and O_2 consumption rate data

Sample ID	Total CO_2 produced (g)	Total CO_2 produced (g)/ starting mass (g)	Total O_2 consumed (g)	Total CO produced (g)
Br Epoxy Laminate, 6 plies, run 1	23.7	0.4	18.3	2.7
Br Epoxy Laminate, 6 plies, run 2	23.4	0.4	17.9	2.5
Br Epoxy Laminate, 6 plies, run 3	20.3	0.3	15.1	2.6
Br Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	8.0	0.7	2.9	0.8
Br Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	6.9	0.7	2.3	0.7
No FR Epoxy Laminate, 6 plies, run 1	35.9	0.6	26.6	1.4
No FR Epoxy Laminate, 6 plies, run 2	39.3	0.6	28.6	2.3
No FR Epoxy Laminate, 6 plies, run 3	37.4	0.6	28.1	1.7
No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	14.6	1.2	5.4	1.0
No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	14.2	1.3	5.3	1.2
Non Hal FR Epoxy Laminate, 6 plies, run 1	29.2	0.5	20.5	2.7
Non Hal FR Epoxy Laminate, 6 plies, run 2	31.7	0.5	22.5	2.7
Non Hal FR Epoxy Laminate, 6 plies, run 3	30.0	0.5	21.0	2.7
Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4	13.0	1.0	3.7	1.4
Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5	11.2	1.0	3.3	1.5

PCDD/Fs and PBDD/Fs Data

For each type of circuit board laminates, combustion product samples from five runs were combined and analyzed to determine total dioxin concentration. The emission levels of Polychlorinated Dibenzo-p-Dioxins and DibenzoFurans (PCDD/Fs) are reported using both ng per Kg of laminate and as ng- Toxic equivalent (TEQ) per Kg of laminate. The TEQ concentration expresses the overall toxicity of a dioxin mixture relative to the toxicity of 2,3,7,8-TeCDD. Each dioxin congener is assigned a toxic equivalent factor (TEF) value based on its relative toxicity to the toxicity of 2,3,7,8- TeCDD [11]. The WHO 2005 TEF values for all 7 dioxin and 10 furan chemical compounds analyzed are presented in Table 7 [12].

Table 7. Toxic Equivalent Factors of Chlorinated Congeners

Isomer.	**2005 WHO (Mammals/Humans) Toxicity Equiv. Factor**
2,3,7,8 - TeCDD	1
1,2,3,7,8 - PCDD	1
1,2,3,4,7,8 - HxCDD	0.1
1,2,3,6,7,8 - HxCDD	0.1
1,2,3,7,8,9 - HxCDD	0.1
1,2,3,4,6,7,8 - HpCDD	0.01
1,2,3,4,6,7,8,9 - OCDD	0.0003
2,3,7,8 - TeCDF	0.1
1,2,3,7,8 - PCDF	0.03
2,3,4,7,8 - PCDF	0.3
1,2,3,4,7,8 - HxCDF	0.1
1,2,3,6,7,8 - HxCDF	0.1
2,3,4,6,7,8 - HxCDF	0.1
1,2,3,7,8,9 - HxCDF	0.1
1,2,3,4,6,7,8 - HpCDF	0.01
1,2,3,4,7,8,9 - HpCDF	0.01
1,2,3,4,6,7,8,9 - OCDF	0.0003

The total TEQ was calculated by summing the multiplication of each congener concentration in the flue gas by its corresponding TEF. The congener concentration (in ng/kg) was calculated from the data obtained from the HRGC/HRMS analysis (in ng/train) and based on the basis of total sampling as shown:

$$Concentration\left(\frac{ng}{kg}\right)$$

$$= \frac{Total\ flow\ rate\ in\ duct}{Flow\ through\ sampling\ line} \times \frac{Total\ congener\ in\ extract\ (ng/train)}{Initial\ mass\ of\ circuit\ board\ \ (kg)}$$

Congeners concentrations below the limit of detection were regarded as zero and reported as less than limit of detection (<LOD).

Due to lack of standards for the analysis of Polybrominated Dibenzo-p-Dioxins and DibenzoFurans (PBDD/Fs) results are semi-quantitative, at best. Since TEFs for PBDD/Fs are not available, the PBDD/F data is only shown in ng per Kg of laminate units.

The results obtained from the analysis of emissions for PCDD/Fs concentrations in the extracts are presented in Table 8 and 9. Most chlorinated congener concentrations were reported as less than the limit of detection. The detected targets appeared to be a carry over from a standard. As expected, the results showed that no chlorinated dioxin/furan congeners were present in combustion exhaust. This confirmed the fact that since chlorine was not present in significant levels in the circuit board laminates, no chlorinated compounds were observed during combustion of the circuit board laminates.

Table 8. Results showing PCDD/Fs concentration in ng- Toxic equivalent (TEQ) per Kg of laminate in the emission samples from combustion of circuit board samples

	TEQ (ng/kg)			
Isomer.	PFR Epoxy laminate	BR FR Epoxy laminate	BR FR Epoxy laminate, repeat run	NFR Epoxy laminate
2,3,7,8 - TeCDD	<LOD	<LOD	<LOD	<LOD
1,2,3,7,8 - PCDD	<LOD	<LOD	13.3	<LOD
1,2,3,4,7,8 - HxCDD	<LOD	<LOD	1.9	<LOD
1,2,3,6,7,8 - HxCDD	<LOD	<LOD	1.3	<LOD
1,2,3,7,8,9 - HxCDD	<LOD	<LOD	2.1	<LOD
1,2,3,4,6,7,8 - HpCDD	<LOD	<LOD	0.3	0.2
1,2,3,4,6,7,8,9 - OCDD	<LOD	<LOD	0.0	0.0
2,3,7,8 - TeCDF	0.8	<LOD	2.7	1.3
1,2,3,7,8 - PCDF	<LOD	<LOD	0.7	<LOD
2,3,4,7,8 - PCDF	<LOD	<LOD	6.7	<LOD
1,2,3,4,7,8 - HxCDF	<LOD	<LOD	3.1	<LOD
1,2,3,6,7,8 - HxCDF	<LOD	<LOD	2.8	<LOD
2,3,4,6,7,8 - HxCDF	<LOD	<LOD	3.7	<LOD
1,2,3,7,8,9 - HxCDF	<LOD	<LOD	4.3	<LOD
1,2,3,4,6,7,8 - HpCDF	<LOD	0.3	0.5	0.1
1,2,3,4,7,8,9 - HpCDF	<LOD	<LOD	0.5	<LOD
1,2,3,4,6,7,8,9 - OCDF	<LOD	<LOD	0.0	<LOD
Total TEQ (ng/kg)	**0.8**	**0.3**	**43.9**	**1.6**

LOD= Limit of Detection
Additional Comments:
PFR Epoxy laminate: detected target appeared to be carry over from a standard
BR FR Epoxy laminate: Sample rerun; elevated standard recoveries were due to a large interfering peak causing reduced signal on the TeCDD recovery standard
BR FR Epoxy laminate, repeat run: All detected targets appeared to be carry over from a standard
NFR Epoxy laminate: All detected targets appeared to be carried over from a standard

Table 9. Results showing PCDD/Fs concentration (in ng/Kg of laminate) in the emission samples from combustion of circuit board samples

Isomer.	**Conc. (ng/kg)**			
	PFR Epoxy laminate	BR FR Epoxy laminate	BR FR Epoxy laminate, repeat run	NFR Epoxy laminate
2,3,7,8 - TeCDD	<LOD	<LOD	<LOD	<LOD
1,2,3,7,8 - PCDD	<LOD	<LOD	13.3	<LOD
1,2,3,4,7,8 - HxCDD	<LOD	<LOD	19.2	<LOD
1,2,3,6,7,8 - HxCDD	<LOD	<LOD	13.3	<LOD
1,2,3,7,8,9 - HxCDD	<LOD	<LOD	20.7	<LOD
1,2,3,4,6,7,8 - HpCDD	<LOD	<LOD	34.0	21.1
1,2,3,4,6,7,8,9 - OCDD	<LOD	<LOD	63.5	33.8
2,3,7,8 - TeCDF	8.1	<LOD	26.6	12.7
1,2,3,7,8 - PCDF	<LOD	<LOD	22.2	<LOD
2,3,4,7,8 - PCDF	<LOD	<LOD	22.2	<LOD
1,2,3,4,7,8 - HxCDF	<LOD	<LOD	31.0	<LOD
1,2,3,6,7,8 - HxCDF	<LOD	<LOD	28.1	<LOD
2,3,4,6,7,8 - HxCDF	<LOD	<LOD	36.9	<LOD
1,2,3,7,8,9 - HxCDF	<LOD	<LOD	42.9	<LOD
1,2,3,4,6,7,8 - HpCDF	<LOD	25.6	51.7	9.9
1,2,3,4,7,8,9 - HpCDF	<LOD	<LOD	48.8	<LOD
1,2,3,4,6,7,8,9 - OCDF	<LOD	<LOD	81.3	<LOD
Total conc. (ng/kg)	**8.1**	**25.6**	**555.6**	**77.5**

LOD= Limit of Detection
Additional Comments:
PFR Epoxy laminate: detected target appeared to be carry over from a standard
BR FR Epoxy laminate: Sample rerun; elevated standard recoveries were due to a large interfering peak causing reduced signal on the TeCDD recovery standard
BR FR Epoxy laminate, repeat run: All detected targets appeared to be carry over from a standard
NFR Epoxy laminate: All detected targets appeared to be carried over from a standard

The results obtained from the analysis of emissions for PBDD/Fs concentrations in the extracts are presented in Table 10. For the PFR laminates and NFR laminates, no brominated congener was detected. The OcBDD and OcBDF compounds were not reported for all circuit boards types because OcBDD/F needed separate clean-up and the $^{13}C_{12}$ labeled OcBDD surrogate standard did not elute from the carbon column during extraction procedure. The data for the BR FR laminates BrFR (first run and repeat run) were consistent. For the first set of experiments, it was found that 3213.8 ng PBDD/Fs per kg of laminates was produced. For the repeat run, it was found that 3389.7 ng PBD/Fs per kg of laminates was produced. No published data on PBDD/Fs concentrations in ng per kg of combustible material burned where found to compare the results.

Table 10. Results showing PBDD/Fs concentration (in ng/Kg of laminate) in the emission samples from combustion of circuit board laminates

	Concentration (ng/kg)			
Isomer.	PFR Epoxy laminate	BR FR Epoxy laminate	BR FR Epoxy laminate, repeat run	NFR Epoxy laminate
2,3,7 TrBDD*	ND	24.4	ND	ND
2,3,7 TrBDF*	ND	ND	ND	ND
2,3,7,8 TeBDD	ND	112.4	88.7	ND
2,4,6,8 TeBDF	ND	172.3	173.0	ND
2,3,7,8 TeBDF	ND	855.4	536.6	ND
1,2,3,7,8 PeBDD	ND	ND	ND	ND
1,2,3,7,8 PeBDF	ND	325.1	300.1	ND
2,3,4,7,8 PeBDF	ND	163.7	112.3	ND
1,2,3,4,7,8/1,2,3,6,7,8 HxBDD	ND	ND	ND	ND
1,2,3,7,8,9 HxBDD	ND	ND	ND	ND
1,2,3,4,7,8 HxBDF	ND	107.5	96.1	ND
1,2,3,4,6,7,9 HpBDD*/**	ND	ND	ND	ND
1,2,3,4,6,7,8 HpBDD*/**	ND	ND	ND	ND
1,2,3,4,6,7,8 HpBDF	ND	1453.0	2082.9	ND
OcBDD	NR	NR	NR	NR
OcBDF	NR	NR	NR	NR
Total conc. (ng/kg)	**-**	**3213.8**	**3389.7**	**-**

*Not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

**Assignment based on the elution order of HpCDD congeners on the DB5 column.

ND= not detected

NR= not reported (OcBDD/F would need separate clean-up; ^{13}C OcBDD did not elute from carbon column)

Heat release data and fire behavior

The combined cone calorimeter heat release data are shown in Table 11. Data for the 6-ply laminate stacks was not reproducible in all aspects of heat and smoke release due to erratic physical effects of burning, which are described below. Data from single ply laminates with one or two strips was also difficult to compare to each other, since the amount of copper metal had some effects on the amount of heat released. It should be noted that for the repeat run for BrFR, heat release data and fire behavior are not provided as they are not impacted by heating of the exhaust duct.

Table 11. Combined Heat Release Rate data

Description	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m2)	Time to Peak HRR (s)	Time to Peak HRR - Tig (s)	Average HRR (kW/m2)	Starting Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m2)	Total smoke Release (m2/m2)	Avg. Effective Heat of Comb. (MJ/kg)	MAHRE (kW/m2)	FIGRA
Br Epoxy Laminate, 6 plies, run 1	3.1	12	242	178	166	68	61.9	19.2	31.0	23.8	2394	12.35	93	1.36
Br Epoxy Laminate, 6 plies, run 2	2.9	14	204	222	208	69	62.2	18.5	29.8	23.4	2019	12.63	75	0.92
Br Epoxy Laminate, 6 plies, run 3	3.0	13	237	208	195	63	60.4	17.6	29.1	19.6	2046	11.06	68	1.14
Br Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	0.4	8	171	20	12	53	11.9	2.5	21.0	3.8	449	15.12	83	8.55
Br Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	0.5	10	185	25	15	43	10.2	2.8	27.4	3.2	424	10.94	76	7.39
No FR Epoxy Laminate, 6 plies, run 1	3.1	14	173	240	226	79	61.5	16.6	27.0	35.5	1401	21.40	96	0.72
No FR Epoxy Laminate, 6 plies, run 2	3.3	15	177	250	235	72	64.5	15.9	24.6	37.9	1350	23.83	85	0.71
No FR Epoxy Laminate, 6 plies, run 3	3.2	17	196	288	271	80	63.8	17.6	27.6	37.5	1310	21.37	88	0.68
No FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 4	0.5	13	379	24	11	97	11.0	3.5	31.9	7.2	329	19.98	138	15.77
No FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 5	0.6	15	265	50	35	81	12.6	3.4	27.0	7.4	353	21.46	111	5.29
Non Hal FR Epoxy Laminate, 6 plies, run 1	3.1	190	152	262	72	64	63.3	14.3	22.6	27.1	1310	18.90	57	0.58
Non Hal FR Epoxy Laminate, 6 plies, run 2	3.2	190	134	326	136	72	64.3	14.9	23.2	30.0	1336	20.13	59	0.41
Non Hal FR Epoxy Laminate, 6 plies, run 3	3.2	206	222	230	24	74	64.5	13.8	21.4	28.0	1209	20.33	59	0.96
Non Hal FR Epoxy Laminate, 1 ply, 2 Cu Strips, run 4	0.5	17	104	29	12	46	12.6	2.2	17.4	4.9	283	22.22	41	3.58
Non Hal FR Epoxy Laminate, 1 ply, 1 Cu Strip, run 5	0.5	15	231	29	14	62	11.0	2.8	25.5	4.5	276	15.47	63	7.96

Along with the heat release data in Table 11, the heat release rate curves are plotted in Figures 8-10. Each of the laminates had their own fire behavior which is described separately below.

Brominated FR Epoxy Laminate Fire Behavior

For the 6-ply laminate stacks, the only reproducible part of the heat release phenomena was the initial ignition and the detection of the 1st HRR peak, given the observed fire behavior of these samples this correlates nicely. Each of the 6 ply laminate stacks, upon exposure to the cone heater, began to smoke within 10 seconds of heat exposure, and then the samples quickly foamed up as a large bubble and ignited. This rapid ignition flashed off quickly and then died back with some edge burning on the top ply, followed by a decrease in heat release. Then the underlying material began to ignite which led to a 2nd HRR peak. These flames continued to grow until all of the remaining plies foamed up and flames began to come out from the sides of the sample. This rapid flare up led to the final HRR peak between 150 and 250 seconds as shown in Figure 8. After this rapid flare up the flames began to die down and eventually the sample extinguished. One sample (HRR-3) actually self extinguished after the 1st HRR peak and reignited after a brief delay (Figure 8 left), again attesting to the physical effects of burning laminate stacks which led to irreproducibility in the HRR curves. Final chars were primarily glass laminate with blackened metal strips. Some soot/char was present on the lower laminates, but the top laminate was a light grey in color and had very little soot/char carbon present. Due to the sample foaming late in the fire, the shutters of the cone calorimeter could not be closed at the end of the test – otherwise the shutters would have crushed the sample residue which would have led to a false load cell (weight loss) result which would have affected many other cone calorimeter measurements. So, after the last flame went out, the sample was allowed to stay under the cone heater for another 60 seconds to collect good baseline data. This change in procedure is noteworthy since it may have burned off the residual carbon on the top ply of the burned laminates since for the single ply laminates, carbon char was found after the sample extinguished. Another thing to note for these samples is that, after ignition and once the flames had grown sufficiently, wherever the sample was burning next to copper, the flames were a bright blue in color, typical for burning of copper salts. The flame color was yellow to orange where there was no copper.

For the single ply laminates (Figure 9 left) the observed behavior of burning was different than that observed with the 6 ply laminate stacks. Upon exposure to the cone heater, the sample rapidly began to smoke, and then quickly foamed up and ignited. The flames grew quickly in intensity and then rapidly extinguished as the epoxy in this thin sample burned away. Final chars were black with carbon/soot noted along with blackened Cu metal strips. There does appear to be some slight difference in HRR behavior for the single and 2 Cu metal strip laminates in that the single Cu strip sample has two peaks of HRR while the double Cu strip sample has only 1 peak of HRR. As described above, blue flames were seen where the sample was burning next to the Cu metal strips.

No Flame Retardant Epoxy Laminate Fire Behavior

The fire behavior of laminates with no flame retardant (control) in the cone calorimeter was very different than that observed for the brominated flame retardant samples. First of all, none of the laminates (either 6 ply or single ply) foamed up upon exposure to the cone heater. Instead, the laminates had a strong tendency to warp and bend up towards the cone heater with snapping and popping heard right before ignition. This behavior was so pronounced for the 6-ply laminates that the cone calorimeter shutters could not be closed when the sample extinguished as the laminate plies had curled up into the space where the shutters would normally close.

Fire behavior of the 6-ply laminates with the non-flame retardant epoxy began with smoke being released shortly after exposure to the heat source (about 12 seconds after start of test) followed shortly thereafter by ignition of the sample. Some blue flames (of lesser blue color intensity than that seen with the brominated FR epoxy laminates) were observed, but for the most part the color of the flames were orange-yellow with some smoke/soot observed at all times. As with the brominated 6-ply stacks, the 6-ply stacks of non-FR epoxy showed irreproducible fire behavior as the top ply would ignite, settle down in heat release/flame intensity, and then the second ply underneath would ignite. Sometimes the top ply would provide sufficient insulation to delay ignition of the underlying plies (see HRR-2 and HRR-3 in Figure 8 right) and in other cases the top ply would deform so much that most of the underlying 2nd ply would be exposed to the cone heater. With all these physical effects of burning, the HRR data for this sample showed a lot more scatter different HRR curve shape, as can be seen in Figure 9 (right). The HRR peak occurred when the bottom 4 plies would finally all ignite at once, leading to a slow rise in heat release followed by a slow steady decrease in HRR whereupon the sample finally extinguished. The final chars from these 6-ply laminates showed very little carbon char; just some soot and the blackened/oxidized copper metal strips.

For the single ply no FR epoxy laminates (Figure 9, right), the samples smoked, began to pop and deform (as seen with the 6 ply laminates) and then rapidly ignited and burned out. No blue flames were observed for these samples when they were burning. As with the 6 ply laminates, the shutters could not be closed at the end of the test due to laminate deformation. The final chars were the same as those observed with the 6-ply laminate stacks, with only fiberglass and blackened metal remaining. Unlike with the single ply brominated FR epoxy laminate HRR data, there is a lot more difference in HRR behavior of 1 Cu metal strip and 2 Cu metal strip HRR data for the non-halogenated FR epoxy laminates (Figure 9 right), but the reason for this major difference is not clear since the observed fire behavior was very similar for both samples. A likely explanation though is that the amount of Cu metal on the surface affected the amount of surface available for burning and pyrolysis.

Non-Halogenated Flame Retardant Epoxy Laminate Fire Behavior

Fire behavior for the non-halogenated flame retardant epoxy laminates (assumed to be phosphorus-based flame retardant) was different than the other two types of epoxy laminates. Phosphorus-based flame retardants in epoxies tend to be condensed phase char formation systems, so that when they burn they convert the carbon-based epoxy “fuel” into graphitic-type protective chars which slow down the rate of mass loss and heat release. Indeed, this type of behavior was observed for the 6-ply laminate stacks, as the samples did ignite rapidly after exposure to the cone heater, but they then extinguished and did not re-ignite for another 150 seconds after the 1st initial ignition (see Figure 10 left). When these laminate stacks were exposed to the cone heater, they smoked and made crackling/popping sounds (caused by delamination) within 10 seconds of exposure to the cone heater. Shortly after that, they ignited, but then the flames died down quickly and the flame went out. The spark igniter was reinserted and eventually the sample reignited. The sample deformed and curled up towards the cone heater towards the end of the test such that the shutters could not be closed at the end of the test. During the burning of the sample, no blue flames were observed, only yellow/orange flames with smoke were seen. At the edges of the sample and towards the end of the test some white colors could be seen at the bottom of the flame, which confirms the presence of phosphorus-based flame retardants. The final chars were black, but the fiberglass could be seen through this black char, which was more than just soot. The copper metal strips were completely blackened. As with the other 6-ply laminate stack data, due to the physical effects during burning, the HRR curve shapes were not very reproducible, but the times to ignition and flameout were reproducible within the cone calorimeter test % error of about 10%.

For the single ply laminates, the effect of the copper strips was more pronounced than that seen with the other samples. The sample with only one copper strip rapidly burned off while the sample with two copper strips did not burn as intensely and took a little longer to burn. Otherwise the fire behavior of this sample was very similar to that of the 6 ply laminate stacks, with the sample smoking and cracking right before ignition, and the laminate curling up towards the cone heater by the end of the test [1].

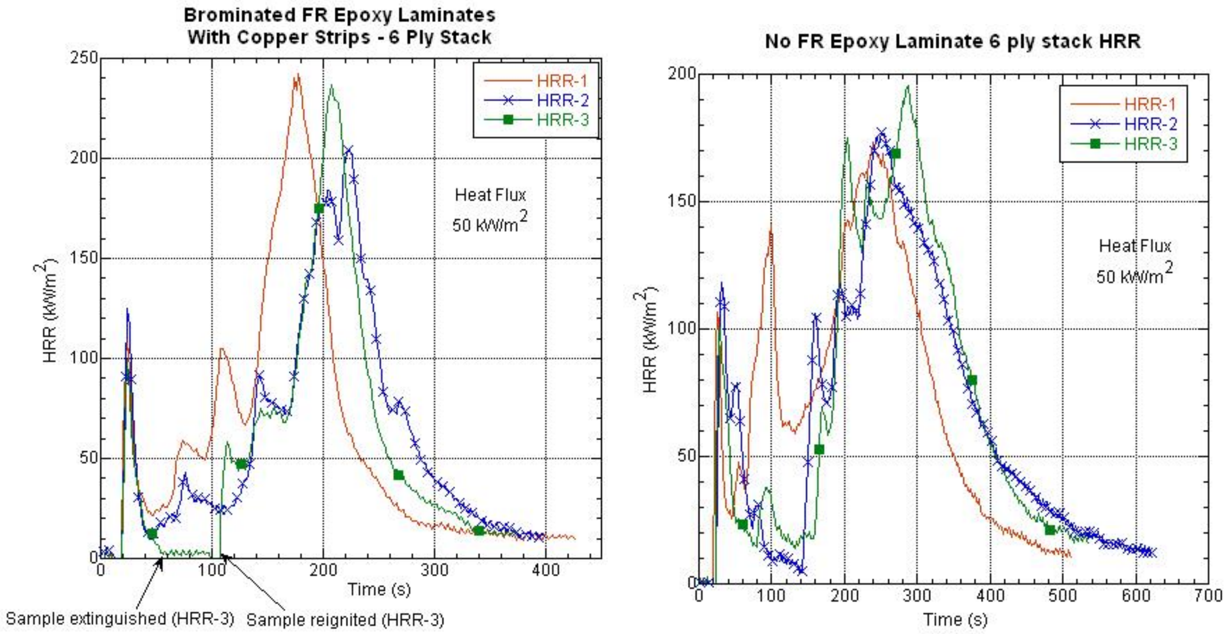


Figure 8. HRR for 6 ply Br Flame Retardant Epoxy Laminate Stacks (left) and No Flame Retardant Epoxy Laminate Stacks (right).

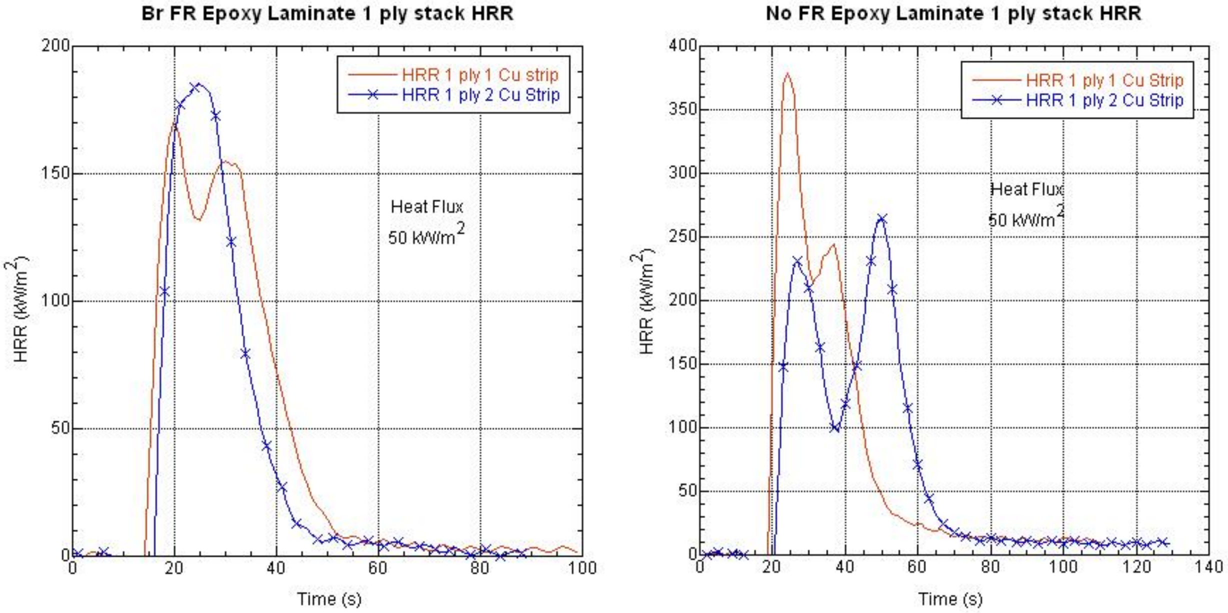


Figure 9. HRR for 1 ply Br Flame Retardant Epoxy Laminates (left) and 1 ply No Flame Retardant Epoxy Laminates (right).

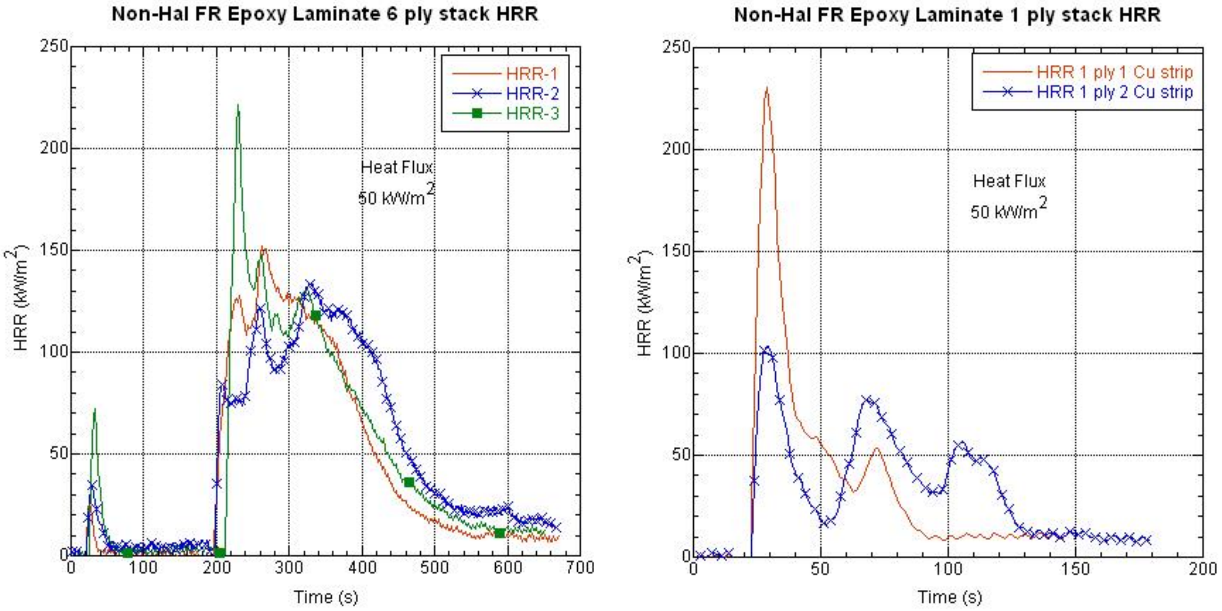


Figure 10. HRR for 6 ply Phosphorous based Flame Retardant Epoxy Laminate Stacks (left) and HRR for 1 ply Phosphorous based Flame Retardant Epoxy Laminates (right).

Conclusion

Laminates' Fire Behavior and Heat Release Data

There are four major conclusions that can be made about these samples from the observed physical fire behavior and from the recorded heat release/smoke release measurements:

1) The 6 ply laminate samples showed erratic HRR behavior due to the physical effects of laminates igniting and curling/foaming/charring at different rates from stack to stack, even with the same material. This type of behavior would be normal for a non-coherent stack of

laminates which would have nothing adhering them together and instead would have air gaps between each ply to allow for additional heat release and secondary fire events to occur.

2) 6-ply laminates showed lower peak HRR compared to single ply laminates. The likely reason for this is that the underlying laminates pull some heat away from the top laminate which makes the 6 ply stack act a little bit more like a thermally thick sample than a thermally thin sample like the single ply laminates. However, it is well known that for the cone calorimeter that sample thickness affects heat release results, and therefore it is not surprising that the peak HRR is higher for the single ply laminates when compared to the 6-ply laminate stacks.

3) The amount of Cu metal on the surface appears to have a slight effect on time to ignition. The more Cu metal present, the more likely that time to ignition will be delayed by a few seconds. This makes sense as the Cu metal can reflect some heat energy back, and, can conduct some of the heat energy out and away from the epoxy laminate. However, the 2-3 second delay in time to ignition, while seen in all of the samples, isn’t significant in regards to overall fire behavior of these materials. Once the single ply laminates ignite, they rapidly go to peak HRR and then extinguish as the fuel is rapidly burned off.

4) Since peak HRR and moment specific data is difficult to compare between samples due to physical effects of burning, it is better to look at total HR and total smoke when comparing between samples. By doing this the following trends appear: Brominated FR epoxy has highest smoke release and lowest total heat release. The non-FR epoxy control has the highest heat release and middle-level smoke release. The non-halogenated FR epoxy has the lowest smoke release (although similar to the non-FR epoxy) and middle level total heat release.

Since the purpose of these experiments was to generate a total amount of material to burn for emissions testing, the total smoke and total heat release data indicate that the experiments were in general a success and that all experiments done did yield a controlled amount of burning material. So while individual specimens tested may not correlate exactly in regards to specific moments of heat release, the total amount of fuel burned/smoke released from specimen to specimen did correlate well, indicating that the cone calorimeter did provide controlled burning specimens over a total amount of sampling time. This is important for the emissions testing since the sampling is done over the total amount of sample burned rather than a specific moment in time of burning [1].

PCDD/Fs and PBDD/Fs emission data

No significant concentrations of PCDD/Fs were found after sampling and analysis of emissions from the combustion of BrFR laminates containing brominated flame retardant, PFR laminates containing non-halogen flame retardant (Phosphorous- based), and NFR laminates containing no-flame retardant. Most targets pollutants were found to be below the limit of detection of the analysis. The targets that were detected appeared to be a carry over from a standard. The results obtained from the analysis of emissions for PBDD/Fs concentrations in the extracts confirmed the presence of pollutants for the combustion of BrFR laminates containing brominated flame retardant. The laminates contained copper strips which could have promoted the formation of dioxins in the emissions. No published data on PBDD/Fs concentrations in ng per kg of combustible material burned was found to compare the results of this study. For the PFR laminates and NFR laminates, no PBDD/F congener was detected.

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APPENDIX I: SAMPLING DATA

Table 1.

Note: All masses are in grams	BFR	NFR	PFR	BFR (repeat)
Mass of cap+container	209.44	209.87	207.68	209.53
Mass of cap+container+water (pre-sampling)	309.78	311.95	308.24	282.99
Mass of cap+container+water (post-sampling)	309.11	310.3	307.36	282.06
(pre-sampling water) - (post-sampling water)	0.67	1.65	0.88	0.93
Mass of cap+container	68.15	68.17	68.15	68.15
Mass of cap+container+silica gel (pre-sampling)	269.06	268.16	268.04	268.35
Mass of cap+container+silica gel (post-sampling)	271.06	270.75	270.93	270.18
Mass of water absorbed in silica gel	**2**	**2.59**	**2.89**	**1.83**
Mass of cap+container	207.9	209.02	208.61	209.05
Mass of cap+container+XAD	247.99	249.09	248.95	249.05
Mass of XAD (pre-sampling)	40.09	40.07	40.34	40
Petri dish	68.24	68.23	68.23	68.23
Petri dish+filter (pre-sampling)	68.66	68.65	68.64	68.65
Mass of filter (pre-sampling)	0.42	0.42	0.41	0.42
Mass of container+cap	209.88	209.13	207.49	208.61
Mass of container+cap+filter (post-sampling)	210.38	209.62	207.99	NA
Mass of filter (post-sampling)	0.5	0.49	0.5	NA
Mass of soot	**0.08**	**0.07**	**0.09**	**NA**

Table 2.

	BFR	NFR	PFR	BFR (repeat)
Soot formed (g)	0.08	0.07	0.09	NA
Mass burned (g)	10.1	12.4	13.9	10.5
soot formed/mass burned (g/g)	0.00792	0.00565	0.00647	NA

Table 3.

	BFR REPEAT				**PFR**			
	Time (h:m:s)	Inside Wall temperature (°C)	Mass (g)	Comments	Time (h:m:s)	Inside Wall temperature (°C)	Mass (g)	Comments
Run 1	0:00:00	95	61.3		0:00:00	96	63.2	
	0:01:44	104	57.4	ignition	0:03:00	95	61.9	
	0:02:44	124	52.1		0:05:00	108	60.3	
	0:03:36	134	44.6	max temp	0:06:00	128	55.3	
	0:04:30	122	43		0:07:15	130	50.5	max temp
	0:05:20	116	42.5		0:08:30	121	48	
	0:06:09	110	42.2	removed	0:09:15	115	47.6	
					0:10:15	110	47	
					0:11:45	106	46.6	
					0:13:40	105	46	removed
Run 2	0:09:34	103	59.8		0:16:35	102	63.8	
	0:09:44	107	58.4	ignition	0:17:37	101	63.1	ignition
	0:10:44	111	56.2		0:19:10	100	62.1	
	0:11:44	127	49.3		0:20:10	117	59.4	re-ignited
	0:12:36	133	43.4	max temp	0:21:10	123	57.3	
	0:13:45	121	41.8		0:22:25	130	52.5	max temp
	0:14:46	116	41.3	removed	0:23:36	128	48.9	
					0:24:36	119	47.9	
					0:25:36	113	47.3	
					0:27:03	109	46.7	
					0:28:31	107	46.4	
					0:30:56	105	45.8	removed
Run 3	0:17:17	107	61		0:33:45	102	64.2	
	0:17:46	109	59.8	ignition	0:34:57	104	63.2	ignition
	0:18:16	109	59.2	re-ignited	0:36:36	102	62	
	0:19:16	119	54.7		0:37:25	107	60.6	re-ignited
	0:20:18	131	46.8	max temp	0:39:03	130	53.1	max temp
	0:21:32	126	42.8		0:40:23	127	49.4	
	0:22:30	118	42.3	removed	0:41:45	118	48.3	
					0:42:50	112	47.9	
					0:44:35	109	47.4	
					0:46:32	107	46.8	removed
Run 4	0:26:40	108	10.4		0:49:12	104	10.6	
	0:27:01	111	9.9	ignition	0:49:42	114	8.4	
	0:27:23	114	7.8	max temp	0:50:20	114	7.7	no flame
	0:27:57	113	9.1	removed	0:52:49	109	7.2	removed
Run	0:31:07	107	11.9		0:55:30	105	12.5	

5	0:31:20	110	10.6		0:57:00	113	9.7	
	0:31:42	114	8.5	max temp	0:57:39	113	10.1	no flame
	0:32:00	113	8.5	removed	0:58:29	110	10	removed

NFR

Time (h:min:sec)	Inside Wall temperature (°C)	Mass (g)	Comments
0:05:31	118	61.1	
0:07:00	127	50.5	
0:08:23	132	46.5	max temp
0:10:00	122	45.1	
0:10:55	117	44.7	
0:11:47	114	44.3	
0:12:51	112	43.8	removed
0:16:09	107	64.2	
0:18:09	113	61.7	
0:19:19	120	58.6	
0:20:32	129	54.3	
0:21:30	131	50.3	max temp
0:22:55	125	47.8	
0:23:58	120	47.1	
0:25:09	116	48.4	
0:26:18	113	47.4	no flame
0:27:44	111	46.2	removed
0:30:46	107	63.6	
0:31:46	111	62	
0:32:45	111	61.2	
0:34:06	126	58.5	
0:35:06	131	54.4	max temp
0:36:41	134	50.6	
0:37:30	128	46.1	
0:38:44	121	45.7	no flame
0:40:08	116	44.8	removed
0:43:39	109	10.8	
0:44:00	121	8	
0:44:22	124	7.1	max temp
0:44:58	120	6.9	
0:45:52	116	6.8	removed
0:49:16	111	12.1	
0:49:32	112	11	
0:50:06	123	8.5	max temp
0:51:00	117	8.6	
0:51:48	114	8.3	removed

Additional Comments

NFR: Stack conditions after experiment:
Outside Wall temperature: 167°C
Inside Wall temperature: 112°C

PFR: Stack conditions after experiment:
Outside Wall temperature: 155°C and 162°C (2 thermocouples on outside wall)
Inside Wall temperature: 74°C

BFR REPEAT : Stack conditions after experiment:
Outside Wall temperature: 158°C and 164°C (2 thermocouples on outside wall)
Inside Wall temperature: 96°C

APPENDIX 2: ANALYSIS DATA

PCDD/Fs:

Pre-extraction surrogate recovery limits:

	Surrogate Recovery limits (range in %)	
13C12-2 MCDF	25.0	130
13C12-2 MCDD	25.0	130
13C12-2,4 DCDF	25.0	130
13C12-2,7 DCDD	25.0	130
13C12-2,4,8 TrCDF	25.0	130
13C12-2,3,7,8 TeCDF	25.0	130
13C12-2,3,7,8 TeCDD	25.0	130
13C12-1,2,3,7,8 PCDF	40.0	130
13C12-1,2,3,7,8 PCDD	40.0	130
13C12-1,2,3,6,7,8 HxCDF	40.0	130
13C12-1,2,3,6,7,8 HxCDD	40.0	130
13C12-1,2,3,4,6,7,8 HpCDF	40.0	130
13C12-1,2,3,4,6,7,8 HpCDD	40.0	130
13C12-1,2,3,4,6,7,8,9 OCDD	25.0	130

Pre- sampling surrogate recovery limits:

	Pre Spike Recovery Limits (range in %)	
13C12-2,8-DCDF	70.0	130
13C12-2,3-DCDD	70.0	130
13C12-2,3,7-TrCDD	70.0	130
37Cl4-2,3,7,8-TeCDD	70.0	130
13C12-2,3,4,7,8-PCDF	70.0	130
13C12-1,2,3,4,7,8-HxCDF	70.0	130
13C12-1,2,3,4,7,8-HxCDD	70.0	130
13C12-1,2,3,4,7,8,9-HpCDF	70.0	130

BR FR Epoxy Laminate:

Sampled: 6/05/08
Extracted: 7/15/08
Acquired: 01/27/09
Sample description/Narrative: Sample Rerun; Elevated Standard Recoveries are due to a large interferent peak causing reduced signal on the TeCDD Recovery Standard.

Pre Extraction Surrogates	**% Recovery**	**Pass or Fail recovery limits**
13C12-2,3,7,8 TeCDF	135.0	F
13C12-2,3,7,8 TeCDD	125.9	P
13C12-1,2,3,7,8 PCDF	108.6	P
13C12-1,2,3,7,8 PCDD	93.4	P
13C12-1,2,3,6,7,8 HxCDF	68.7	P
13C12-1,2,3,6,7,8 HxCDD	65.3	P
13C12-1,2,3,4,6,7,8 HpCDF	59.6	P
13C12-1,2,3,4,6,7,8 HpCDD	78.6	P
13C12-1,2,3,4,6,7,8,9 OCDD	67.3	P

Pre-Sampling Surrogates	**% Recovery**	**Pass or Fail recovery limits**
37Cl4-2,3,7,8-TeCDD	91.3	P
13C12-2,3,4,7,8-PCDF	91.8	P
13C12-1,2,3,4,7,8-HxCDF	108.1	P
13C12-1,2,3,4,7,8-HxCDD	112.9	P
13C12-1,2,3,4,7,8,9-HpCDF	112.7	P

Isomer.	**ng/train**		**2005 WHO (Mammal/Humans) Toxicity Equiv. Factor**	**TEQ ng/train**
2,3,7,8 - TeCDD	0.029	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.095	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.113	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.103	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.113	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.196	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDD	0.231	LOD	0.0003	0.00000
2,3,7,8 - TeCDF	0.03	LOD	0.1	0.00000
1,2,3,7,8 - PCDF	0.064	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.064	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.032	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.029	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.036	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.04	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.084		0.01	0.00084
1,2,3,4,7,8,9 - HpCDF	0.064	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.131	LOD	0.0003	0.00000

ND = not detected	EMPC=Est. Max. Possible Concentration	**Total TEQ ng/train**	**0.0008**
NS= not spiked	LOD=Limit of Detection		

NFR Epoxy Laminate:

Sampled: 6/16/08
Extracted: 7/15/08
Acquired: 12/15/08
Sample description/Narrative: All detected targets appear to be carry over from a Standard.

Pre Extraction Surrogates	**% Recovery**	**Pass or Fail recovery limits**
13C12-2,3,7,8 TeCDF	88.1	P
13C12-2,3,7,8 TeCDD	88.0	P
13C12-1,2,3,7,8 PCDF	97.4	P
13C12-1,2,3,7,8 PCDD	101.8	P
13C12-1,2,3,6,7,8 HxCDF	75.9	P
13C12-1,2,3,6,7,8 HxCDD	73.6	P
13C12-1,2,3,4,6,7,8 HpCDF	67.9	P
13C12-1,2,3,4,6,7,8 HpCDD	85.1	P
13C12-1,2,3,4,6,7,8,9 OCDD	72.4	P

Pre-Sampling Surrogates	**% Recovery**	
37Cl4-2,3,7,8-TeCDD	90.0	P
13C12-2,3,4,7,8-PCDF	100.9	P
13C12-1,2,3,4,7,8-HxCDF	104.2	P
13C12-1,2,3,4,7,8-HxCDD	111.1	P
13C12-1,2,3,4,7,8,9-HpCDF	115.5	P

Isomer.	**ng/train**		**2005 WHO (Mammals/Humans) Toxicity Equiv. Factor**	**TEQ ng/train**
2,3,7,8 - TeCDD	0.013	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.015	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.024	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.022	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.024	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.06		0.01	0.00060
1,2,3,4,6,7,8,9 - OCDD	0.096		0.0003	0.00003
2,3,7,8 - TeCDF	0.036		0.1	0.00360
1,2,3,7,8 - PCDF	0.014	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.014	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.018	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.016	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.02	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.022	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.028		0.01	0.00028
1,2,3,4,7,8,9 - HpCDF	0.025	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.063	LOD	0.0003	0.00000

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection

Total TEQ ng/train **0.0045**

PFR Epoxy Laminate:

Sampled: 06/17/08
Extracted: 07/15/08
Date Acquired: 12/15/08
Sampled description/ Narrative: All detected targets appear to be carry over from a Standard.

Pre Extraction Surrogates	**% Recovery**	**Pass or Fail recovery limits**
13C12-2,3,7,8 TeCDF	90.0	P
13C12-2,3,7,8 TeCDD	89.4	P
13C12-1,2,3,7,8 PCDF	109.9	P
13C12-1,2,3,7,8 PCDD	110.9	P
13C12-1,2,3,6,7,8 HxCDF	70.4	P
13C12-1,2,3,6,7,8 HxCDD	69.2	P
13C12-1,2,3,4,6,7,8 HpCDF	64.4	P
13C12-1,2,3,4,6,7,8 HpCDD	80.2	P
13C12-1,2,3,4,6,7,8,9 OCDD	72.5	P

Pre-Sampling Surrogates	**% Recovery**	**Pass or Fail recovery limits**
37Cl4-2,3,7,8-TeCDD	105.3	P
13C12-2,3,4,7,8-PCDF	115.5	P
13C12-1,2,3,4,7,8-HxCDF	119.9	P
13C12-1,2,3,4,7,8-HxCDD	128.5	P
13C12-1,2,3,4,7,8,9-HpCDF	135.2	F

Isomer.	**ng/train**		**2005 WHO (Mammals/Humans) Toxicity Equiv. Factor**	**TEQ ng/train**
2,3,7,8 - TeCDD	0.012	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.015	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.025	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.023	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.025	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.036	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDD	0.047	LOD	0.0003	0.00000
2,3,7,8 - TeCDF	0.024	EMPC	0.1	0.00240
1,2,3,7,8 - PCDF	0.013	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.013	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.014	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.013	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.016	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.018	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.015	LOD	0.01	0.00000
1,2,3,4,7,8,9 - HpCDF	0.02	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.047	LOD	0.0003	0.00000
ND = not detected	EMPC=Est. Max. Possible Concentration		**Total TEQ**	
NS= not spiked	LOD=Limit of Detection		**ng/train**	**0.0024**

BR FR Epoxy Laminate repeat run:

Sampled: 06/18/08
Extracted: 07/15/08
Acquired: 12/09/08
Sampled description/ Narrative: All detected targets appear to be carry over from a Standard.

Pre Extraction Surrogates	**% Recovery**	**Pass or Fail recovery limits**
13C12-2,3,7,8 TeCDF	109.5	P
13C12-2,3,7,8 TeCDD	114.9	P
13C12-1,2,3,7,8 PCDF	112.3	P
13C12-1,2,3,7,8 PCDD	110.2	P
13C12-1,2,3,6,7,8 HxCDF	52.2	P
13C12-1,2,3,6,7,8 HxCDD	56.6	P
13C12-1,2,3,4,6,7,8 HpCDF	47.9	P
13C12-1,2,3,4,6,7,8 HpCDD	55.4	P
13C12-1,2,3,4,6,7,8,9 OCDD	49.2	P

Pre-Sampling Surrogates	**% Recovery**	**Pass or Fail recovery limits**
37Cl4-2,3,7,8-TeCDD	96.4	P
13C12-2,3,4,7,8-PCDF	100.9	P
13C12-1,2,3,4,7,8-HxCDF	120.5	P
13C12-1,2,3,4,7,8-HxCDD	126.4	P
13C12-1,2,3,4,7,8,9-HpCDF	127.2	P

Isomer.	**ng/train**		**2005 WHO (Mammals/Humans) Toxicity Equiv. Factor**	**TEQ ng/train**
2,3,7,8 - TeCDD	0.036	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.036		1	0.03600
1,2,3,4,7,8 - HxCDD, co-elution	0.052		0.1	0.00520
1,2,3,6,7,8 - HxCDD	0.036		0.1	0.00360
1,2,3,7,8,9 - HxCDD	0.056		0.1	0.00560
1,2,3,4,6,7,8 - HpCDD	0.092		0.01	0.00092
1,2,3,4,6,7,8,9 - OCDD	0.172		0.0003	0.00005
2,3,7,8 - TeCDF	0.072		0.1	0.00720
1,2,3,7,8 - PCDF	0.06		0.03	0.00180
2,3,4,7,8 - PCDF	0.06		0.3	0.01800
1,2,3,4,7,8 - HxCDF	0.084		0.1	0.00840
1,2,3,6,7,8 - HxCDF	0.076		0.1	0.00760
2,3,4,6,7,8 - HxCDF	0.1		0.1	0.01000
1,2,3,7,8,9 - HxCDF	0.116		0.1	0.01160
1,2,3,4,6,7,8 - HpCDF	0.14		0.01	0.00140
1,2,3,4,7,8,9 - HpCDF	0.132		0.01	0.00132
1,2,3,4,6,7,8,9 - OCDF	0.22		0.0003	0.00007
ND = not detected	EMPC=Est. Max. Possible Concentration		**Total TEQ**	
NS= not spiked	LOD=Limit of Detection		**ng/train**	**0.1188**

Blank run:

Sampled: 05/29/08
Extracted: 07/15/08
Acquired: 01/27/09
Sample Description/ Narrative: sample rerun.

Pre Extraction Surrogates	**% Recovery**	**Pass or Fail recovery limits**
13C12-2,3,7,8 TeCDF	90.6	P
13C12-2,3,7,8 TeCDD	86.3	P
13C12-1,2,3,7,8 PCDF	78.5	P
13C12-1,2,3,7,8 PCDD	79.8	P
13C12-1,2,3,6,7,8 HxCDF	73.6	P
13C12-1,2,3,6,7,8 HxCDD	72.2	P
13C12-1,2,3,4,6,7,8 HpCDF	66.1	P
13C12-1,2,3,4,6,7,8 HpCDD	86.0	P
13C12-1,2,3,4,6,7,8,9 OCDD	77.1	P

Pre-Sampling Surrogates	**% Recovery**	**Pass or Fail recovery limits**
37Cl4-2,3,7,8-TeCDD	100.9	P
13C12-2,3,4,7,8-PCDF	112.8	P
13C12-1,2,3,4,7,8-HxCDF	118.4	P
13C12-1,2,3,4,7,8-HxCDD	122.2	P
13C12-1,2,3,4,7,8,9-HpCDF	109.2	P

Isomer.	**ng/train**		**2005 WHO (Mammals/Humans) Toxicity Equiv. Factor**	**TEQ ng/train**
2,3,7,8 - TeCDD	0.026	LOD	1	0.00000
1,2,3,7,8 - PCDD, co-elution	0.043	LOD	1	0.00000
1,2,3,4,7,8 - HxCDD, co-elution	0.061	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDD	0.056	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDD	0.061	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDD	0.129	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDD	0.152	LOD	0.0003	0.00000
2,3,7,8 - TeCDF	0.029	LOD	0.1	0.00000
1,2,3,7,8 - PCDF	0.033	LOD	0.03	0.00000
2,3,4,7,8 - PCDF	0.033	LOD	0.3	0.00000
1,2,3,4,7,8 - HxCDF	0.033	LOD	0.1	0.00000
1,2,3,6,7,8 - HxCDF	0.03	LOD	0.1	0.00000
2,3,4,6,7,8 - HxCDF	0.036	LOD	0.1	0.00000
1,2,3,7,8,9 - HxCDF	0.041	LOD	0.1	0.00000
1,2,3,4,6,7,8 - HpCDF	0.036	LOD	0.01	0.00000
1,2,3,4,7,8,9 - HpCDF	0.048	LOD	0.01	0.00000
1,2,3,4,6,7,8,9 - OCDF	0.113	LOD	0.0003	0.00000

ND = not detected	EMPC=Est. Max. Possible Concentration		**Total TEQ**	
NS= not spiked	LOD=Limit of Detection		**ng/train**	**ND**

PBDD/Fs:

BR FR Epoxy Laminate:

Sampled: 6/05/08
Extracted: 7/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	**% Recovery**
13C 237 TrBDD (IS)	87.0
13C 2378 TeBDD (IS)	56.4
13C 123678 HxBDD (IS)	115.1
13C 123789 HxBDD (IS)	96.3
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	123.7
13C 12378 PeBDD (DSSP)	127.9

Isomer	**ng/train**
237 TrBDD*	0.08
237 TrBDF*	ND
2378 TeBDD	0.37
2468 TeBDF	0.56
2378 TeBDF	2.80
12378 PeBDD	ND
12378 PeBDF	1.06
23478 PeBDF	0.54
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	0.35
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	4.76
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

NFR Epoxy Laminate:

Sampled: 6/16/08
Extracted: 7/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	**% Recovery**
13C 237 TrBDD (IS)	108.9
13C 2378 TeBDD (IS)	89.7
13C 123678 HxBDD (IS)	132.8
13C 123789 HxBDD (IS)	102.4
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	103.7
13C 12378 PeBDD (DSSP)	113

Isomer	**ng/train**
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	ND
2468 TeBDF	ND
2378 TeBDF	ND
12378 PeBDD	ND
12378 PeBDF	ND
23478 PeBDF	ND
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	ND
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	ND
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

PFR Epoxy Laminate:

Sampled: 06/17/08
Extracted: 07/15/08
Date Acquired: 12/15/08

Pre Extraction Surrogates	% Recovery
13C 237 TrBDD (IS)	79.6
13C 2378 TeBDD (IS)	61.1
13C 123678 HxBDD (IS)	122.6
13C 123789 HxBDD (IS)	116.1
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	117.6
13C 12378 PeBDD (DSSP)	139.1

Isomer	ng/train
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	ND
2468 TeBDF	ND
2378 TeBDF	ND
12378 PeBDD	ND
12378 PeBDF	ND
23478 PeBDF	ND
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	ND
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	ND
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

BR FR Epoxy Laminate repeat run:

Sampled: 06/18/08
Extracted: 07/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	**% Recovery**
13C 237 TrBDD (IS)	77.2
13C 2378 TeBDD (IS)	57.1
13C 123678 HxBDD (IS)	112.5
13C 123789 HxBDD (IS)	120.9
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	110.5
13C 12378 PeBDD (DSSP)	139.6

Isomer	**ng/train**
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	0.24
2468 TeBDF	0.47
2378 TeBDF	1.45
12378 PeBDD	ND
12378 PeBDF	0.81
23478 PeBDF	0.30
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	0.26
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	5.64
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

Blank run:

Sampled: 07/15/08
Extracted: 07/16/08
Acquired: 02/17/09

Pre Extraction Surrogates	% Recovery
13C 237 TrBDD (IS)	117.3
13C 2378 TeBDD (IS)	93.5
13C 123678 HxBDD (IS)	118.1
13C 123789 HxBDD (IS)	106.0
13C OcBDD (IS)	NR
13C 2468 TeBDF (DSSP)	105.3
13C 12378 PeBDD (DSSP)	112.1

Isomer	ng/train
237 TrBDD*	ND
237 TrBDF*	ND
2378 TeBDD	ND
2468 TeBDF	ND
2378 TeBDF	ND
12378 PeBDD	ND
12378 PeBDF	ND
23478 PeBDF	ND
123478/123678 HxBDD	ND
123789 HxBDD	ND
123478 HxBDF	ND
1234679 HpBDD*/**	ND
1234678 HpBDD*/**	ND
1234678 HpBDF	ND
OcBDD	NR
OcBDF	NR

** not present in the standard; assignment based on isotope theoretical ratios and retention times of matching internal standards and native*

congeners; quantified based on concentration of the congeners of the same bromination level present in the standard

*** assignment based on the elution order of HpCDD congeners on the DB5 column*

ND = not detected

NS= not spiked

EMPC=Est. Max. Possible Concentration

LOD=Limit of Detection (S/N=3)

NR=not reported (OcBDD/F would need separate clean-up;13C OcBDD did not elute from carbon column)

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX C

U.S. EPA. Analysis of Circuit Board Samples by XRF. Original Report - July 28, 2008. Revised Report - March 23, 2009. Prepared by Arcadis.

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Analysis of Circuit Board Samples by XRF

Report

Original Report - July 28, 2008
Revised Report - March 23, 2009

DISCLAIMER: The USEPA Design for the Environment Program has provided additional information in Appendix B and Appendix C to further explain methods and results. This information is critical for interpreting the main report, especially in regards to chorine measurements. Results found in the main report are not complete without the information in the appendices, and cannot be correctly understood or interpreted without their aid.

ARCADIS

Analysis of Circuit Board Samples by XRF

Report

Prepared for:

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Tables

Figures

Appendices

Appendix A: Responses to Questions

Appendix B: Laminate Etching and Chlorine Measurements

Appendix C: ISOLA Experiment Demonstrating the Impact of the Etching Process on Chlorine Measurements

1. Statement of Work

The following report is in response to a task under Work Assignment (WA) No. 3-37, that consisted of an elemental analysis of two sets of circuit boards samples by X-ray Fluorescence (XRF) Spectrometry. This report describes the results of those analyses and provides discussions of several questions that have arisen from these analyses.

2. Introduction

Under two separate events, described as “Phase 1” and “Phase 2,” circuit board samples were received for analyses. Table 1 presents this information.

Table 1: Samples Received

Laminate #	**Phase**	Laminate type
1	1	NFR
2	1	BFR
3	1	PFR
4	2	HF
5	2	HF
6	2	HF
7	2	HF

NFR : Non-flame Retardant ; BFR: Bromine Flame Retardant ; PFR: Phosphorous Flame Retardant ;   HF: Halogen-free

Each board was received “mostly” free of copper plating. Phase 2 samples were accompanied by a letter that indicated 12” by 12” samples of “halogen-free laminates.” Inspection of each showed a rectangular area of plated copper in one corner of each sample that was used to identify each sample. Further inspection showed that some samples had additional small, random areas of elemental copper. This was also true of the phase 1 samples.

3. Experimental

3.1 Sample preparation

3.1.1 Phase 1

As directed, phase 1 samples were cored in the shop at random locations. These circuit board disks were sized to be a slip fit to our standard sample cups. Separate disks were cut for each individual analysis.

3.1.2 Phase 2

As agreed prior to sample receipt, samples were homogenized, powdered, pelletized, and analyzed by XRF. One sample was prepared and analyzed in duplicate. One spiked sample was prepared and analyzed.

3.1.2.1 Sub-sampling

To minimize the errors of heterogeneity, each board was sub-sampled from several locations. One board was weighed at ~ 79 g. per square foot. To ensure that any one sample was of sufficient size to provide sufficient material for sample, replicate, and spike, it was decided to sample 21-1” diameter locations in a representative manner. Boards were delivered to the shop, which laid out a 9 by 7 grid. With directions to avoid potential elemental copper, all edge areas were not sampled. 21 of the remaining 35 positions were sampled by coring.

3.1.2.2 Milling

The 21 disks from each sample were homogenized by milling. A Spex Certiprep model 6850 Freezer/Mill was used for this step. This instrument is basically a hammer mill operating at liquid nitrogen temperatures. All 21 disks were added to a sample tube along with the stainless steel, SS, hammer. This instrument has the capacity to handle a single sample of this size. Table 2 provides the operating parameters for the first milling operation.

Table 2: Milling parameters

Operation	Value
Pre-cool time	15 min.
# of cycles	4
Milling time	3 min.
Re-cool time	10 min.

After samples had warmed back to room temperature, they were opened and examined. The milling was considered generally acceptable, with a large fraction of the sample present as powder. A fraction of each sample, however, was present as large flakes. Figure 1 shows one sample after size classification.

Figure 1 . Sieved Circuit Board

It was unclear whether this coarse flake fraction (left) represented a surface treatment coating or was merely incomplete milling of a homogeneous sample. After discussions it was decided to sieve, re-mill the coarse fraction, and combine. A W.S. Tyler Number 18 sieve, Tyler Equivalent 16 mesh, was used for the fractionation. The fine fraction was transferred to a pre-cleaned 40 mL sample vial while the coarse fraction was returned to the cryo-mill for further milling. Table 3 provides the operating parameters for this second milling operation.

Table 3. Coarse fraction Milling Parameters

Operation	Value
Pre-cool time	10 min.
# of cycles	4
Milling time	2 min.
Re-cool time	5 min.

Less stringent conditions were used since the coarse fraction represented a smaller sample. Coarse fractions were found to range between ~ 1 g and 3 g. This second milling operation was successful and the sample fractions were combined.

3.1.2.3 Homogenization and sub-sampling

Sample homogenization began with the coring of multiple discs spanning the area of each sample. It continued with the cryo-milling operation described in the previous section. It was finalized just prior to sample weighing by sample riffling. A Humboldt Mfg. Co. Model H-3971C archeological grade riffler was used for this purpose. This model was designed for samples in the several gram range. A riffler has the purpose of sub-sampling a larger powdered sample in a statistically equivalent manner that is particle-size and density independent. It achieves this by fractionating the total sample through multiple, equivalently sized paths leading to two or more sample buckets. No assumptions, however, can be made that the sub-samples will remain equivalent if time is allowed to pass. Riffling must be done immediately prior to sample use.

This riffler is manufactured of SS (stainless steel). It consists of a hopper, a gate, multiple equivalent alternating vertically angled slots, and two buckets. It may be used for both homogenization and sub-sampling and was used for both purposes in this project. The entire sample was passed through the riffler twice. After the second pass, sample material in one bucket was returned to the sample vial. The sub-sample in the second bucket represented ~ 4 g at this point. This fraction was passed through the riffler one more time. Each bucket contained about 2 g, which was the correct size for preparing a single XRF pellet.

3.1.2.4 Pellet Preparation

Pellets were prepared by pressing a mixture of powdered sample with a polymeric binder. 2 grams of sample were weighed and transferred to a boron carbide mortar and pestle. The sample was ground for a period, though little grinding took place at this stage for these samples. 2 mL of Spex Liquid Binder, equivalent to 200 mg of binder in a dichloromethane carrier, were added using a Gilson Microman positive displacement pipettor. Sample was mixed until the sample returned to a free-flowing state. Sample was transferred to 32 mm dies with vacuum port. Pellet was pressed under vacuum in a Spex 3630 X-press programmable hydraulic press. Table 4 presents the pelletizing parameters.

Table 4. Pellet Press Parameters

Operation	Value
Applied pressure	20 tons
Hold time	1.1 min.
Release time	1.0 min.

Formed pellets were transferred to Millipore 47 mm Petrislides for identification and stored in a silica gel controlled desiccator until ready for analysis.

As agreed, one sample was prepared in duplicate. As agreed, one sample was spiked with known masses during the pellet preparation stage. After discussions with the work assignment manager and the industry committee, spiking materials and elements were selected as described in the next section. Based upon data from the first set of circuit boards; spikes were prepared for aluminum, calcium, and copper.

3.1.2.5 Preparation of Spiked Sample

As directed, one sample was prepared by spiking with known masses of certain analytes to provide data on recovery. Sample 7 was chosen since that sample represents the most complete data set. In other words, sample 7 was prepared in duplicate and analyzed in replicate. This sample had the most data available for comparison to the spiked sample.

Based upon data from the Phase 1 circuit boards; spikes were prepared for aluminum, calcium, and copper using reagent grades of Al_2O_3, $CaCO_3$, and $CuSO_4$, respectively. This gave us data on a fourth element; S. Table 5 provides data on the preparation of the spiked sample.

Table 5. Composition of Spiked Sample 7

Material	Mass, g
Sample 7	1.761
Al_2O_3	0.0383
$CaCO_3$	0.1504
$CuSO_4$	0.0505
Total	2.0002

The four materials listed in Table 5 were weighed in the amounts described in Table 5 and mixed manually using mortar and pestle. A pellet was prepared from this mix as described in the previous section.

3.2 Analysis

Pressed sample pellets were analyzed on a Panalytical model PW2404 wavelength dispersive X-Ray Fluorescence Spectrometer equipped with the PW2540 sample changer. The instrument is equipped with both flow and scintillation detectors plus five crystals. The instrument is controlled and acquires data using the manufacturer's software, ***SuperQ***. The entire spectrum is acquired as 10 sub-scans using variations in applied power, crystal, detector, filter material, and goniometer setting.

Data were acquired using the application, ***IQ+Metalloids***. ***IQ+Metalloids*** is a variation of the manufacturer supplied application, ***ZIQ+***. ***IQ+Metalloids*** adds 4 channels to provide increased sensitivity for the elements: arsenic, selenium, mercury, and lead. The increased sensitivity comes from increased counting times while the goniometer sits at the peak maxima. ***ZIQ+*** is a full scan application, which optimizes sample throughput.

3.3 Quantification

Data acquired as above are quantified using the manufacturer supplied software, ***IQ+***. ***IQ+*** is a matrix independent, fundamental parameters based quantification program.

4. Data

4.1 Phase 1

Table 6 presents the data for the three Phase 1 samples. Each was analyzed in duplicate; where each analysis also represents a replicate sample preparation (cores from different locations on the board). To be explicit, due to sample decomposition within the instrument, each sample core was analyzed once. During analysis, the whole-board cores charred. Replicate analysis on charred samples seemed neither good chemistry nor good for the instrument.

Table 6. Results for Phase 1 Samples

Sample	**1-NFR**		**2-BFR**		**3-PFR**	
Element	**Mean, %**	**% RSD**	**Mean, %**	**% RSD**	**Mean, %**	**% RSD**
Na	0.109	1.76	0.01		0.114	67.47
Mg	0.008	5.38			0.0070	
Al	0.083	31.94	1.042		0.773	5.50
Si	0.398	37.02	0.145	2.34	0.201	8.84
P	0.0016	16.26	0.0017	23.03	4.19	1.75
S	0.010	14.89	0.0081	60.67	0.013	8.03
Cl	0.878	9.91	0.591	42.27	0.517	11.30
K	0.0078	27.70	0.0043		0.0070	49.55
Ca	2.62	10.04	1.29	33.60	2.49	4.67
Ti	0.061	9.09	0.038	25.42	0.060	4.20
Cr	0.0039				0.0044	
Fe	0.036	9.69	0.033	28.74	0.038	2.30
Cu	0.054	1.03	1.81	137.65	3.59	13.93
As	0.0008	17.32	0.056	27.16	0.0011	
Br			6.13	22.53	0.0047	12.49
Sr	0.064	4.72	0.064	28.89	0.083	1.08
Pb	0.0007	30.44			0.0007	
Zr			0.0088			

NFR : Non-flame Retardant ; BFR: Bromine Flame Retardant ; PFR: Phosphorous Flame Retardant ; HF: Halogen-free

Results above are the average of duplicate samples; reproducibility is also presented as % relative standard deviation, % RSD. In Table 6, an empty cell under a Mean column heading indicates that this element was not detected in either replicate of this sample. An empty cell under % RSD indicates that the element was only observed in one of the replicates of that sample.

In examining Table 6, the most striking feature is the very large % RSDs found for several results. This is true for all three samples. This is attributed to circuit board heterogeneity.

4.2 Phase 2

Table 7 presents the data acquired under this task. Colored cells represent not detected elements for the respective samples.

The first pellet (sample 7) was analyzed three times within a 1 hour period to provide data on short term reproducibility. These data are provided in Table 8.

As directed, one sample was selected for replicate sample preparation and analyses. These data may be found in Table 9. Here, both “Replicate 1” and “Replicate 2” represent the mean determinations of triplicate data collections on a single pellet.

The results for sample 7 spiked as described in Table 5 are provided in Table 10. For comparison the results from replicate preparations of sample 7 are repeated from Table 9.

Table 7. Elemental Concentrations, weight %

Element	4	5	6	7
F	🟨	🟨	🟨	0.054
Na	0.135	0.143	0.121	0.151
Mg	0.663	0.085	0.410	0.375
Al	2.76	5.65	6.35	5.30
Si	15.65	9.23	7.77	10.07
P	1.42	0.84	0.74	0.68
S	0.0104	0.0050	0.0049	0.0098
Cl	0.449	0.427	0.488	1.044
K	0.0161	0.0126	0.0087	0.0123

Element	4	5	6	7
Ca	5.39	4.58	4.47	5.64
Ti	0.107	0.096	0.093	0.117
Cr	0.0184	0.0045	0.0058	0.0065
Fe	0.135	0.067	0.064	0.088
Ni	0.0044			
Cu	0.051	0.041	0.047	0.056
Zn	0.0050	0.0031	0.0044	0.0043
Br		0.0012		0.0012
As			0.00071	0.00116
Sr	0.0616	0.0627	0.0581	0.0722
Zr	0.0038			
Ba			0.0168	
Pb	0.00084			0.00087

Table 8. Sample 7, Short Term Reproducibility, weight %

Element	Rep 1	Rep 2	Rep 3	Mean	% RSD
F			0.05028	0.05028	
Na	0.148	0.1447	0.1473	0.146667	1.19
Mg	0.3678	0.3776	0.3834	0.376267	2.10
Al	5.305	5.253	5.325	5.294333	0.70
Si	9.97	9.972	10.04	9.994	0.40
P	0.6837	0.6793	0.6879	0.683633	0.63
S	0.0122	0.008915	0.00974	0.010285	16.62
Cl	0.9215	0.8356	0.813	0.8567	6.68
K	0.01335	0.01237	0.01404	0.013253	6.33
Ca	5.659	5.674	5.614	5.649	0.55
Ti	0.1199	0.1182	0.114	0.117367	2.59
Cr	0.006383	0.007127	0.006177	0.006562	7.62
Fe	0.09025	0.09096	0.09163	0.090947	0.76
Ni					
Cu	0.059	0.05484	0.05479	0.05621	4.30
Zn	0.00449	0.003899	0.00459	0.004326	8.63
Br	0.001292	0.001128	0.001084	0.001168	9.39
As					
Sr	0.072	0.07354	0.07197	0.072503	1.24
Zr					
Ba					
Pb	0.000619	0.000709	0.001066	0.000798	29.65

Table 9. Sample Preparation Reproducibility, Sample 7

Element	Replicate 1	Replicate 2	Mean	% RSD
F	0.0503	0.0570	0.0537	8.91
Na	0.1467	0.1558	0.1513	4.29
Mg	0.3763	0.3731	0.3747	0.60
Al	5.294	5.302	5.298	0.10
Si	9.994	10.143	10.069	1.05
P	0.6836	0.6713	0.6774	1.29
S	0.01029	0.00934	0.00981	6.84
Cl	0.86	1.23	1.04	25.36
K	0.0133	0.0113	0.0123	11.40
Ca	5.649	5.625	5.637	0.30
Ti	0.11737	0.11597	0.11667	0.85
Cr	0.00656	0.00653	0.00655	0.32
Fe	0.09095	0.08504	0.08799	4.75
Ni				
Cu	0.05621	0.05573	0.05597	0.61
Zn	0.00433	0.00428	0.00430	0.74
Br	0.0012	0.0012	0.0012	0.00
As		0.0012	0.0012	
Sr	0.07250	0.07199	0.07225	0.50
Zr				
Ba				
Pb	0.00080	0.00095	0.00087	12.38

Table 10. Recovery of Spikes, Sample 7, weight %

Element	Sample 7 Mean (Table 9)	Sample 7 Spike	Mean % Recovery	Recovery % RSD
Al	5.298	5.193333	91	0.5
Ca	5.637	8.201	103	0.9
Cu	0.05597	1.019333	97	1.3
S	0.00981	0.614233	119	2
F	0.0537			
Na	0.1513	0.147767	111	4
Mg	0.3747	0.293467	89	0.4
Si	10.069	8.333	94	0.5
P	0.6774	0.5176	87	0.5
Cl	1.04	0.846133	92	8
K	0.0123	0.010305	95	2
Ti	0.11667	0.100767	98	2
Cr	0.00655	0.006422	111	15
Fe	0.08799	0.072413	93	2
Ni				
Zn	0.00430	0.004176	110	5
Br	0.0012	0.001184	115	0
As	0.0012	0.00118	115	23
Sr	0.07225	0.066293	104	1.2
Zr				
Ba				
Pb	0.00087	0.000601	78	15

The spiking of a non-blank material provides results that are slightly difficult to interpret. The spiked material acts as a diluent for all elemental results that are not added as part of the spiking process. Iron and magnesium in Table 10 are an example of this.

The proper calculation is described by equations 1 and 2.

$$\%Theoretical\,Recovery_i = 100 * \frac{\frac{\%analyte_i * Sample7}{100} + \sum GRAV_{ij} * Spike_j}{Sample7 + \sum Spike_j} \qquad \text{Equation 1}$$

$$\%Spike\,Recovery = 100 * \frac{\%SpikedSample_i}{\%Theoretical\,Recovery_i} \qquad \text{Equation 2}$$

Where sample 7 and $Spike_j$ refer to the values found in Table 5, %analyte values are found in the first column of Table 9. $GRAV_{ij}$ refers to the gravimetric factor for analyte i in spike material j.

To be more explicit, one example of $Spike_j$ from Table 5 would be Al_2O_3. The only $analyte_i$ in alumina would be aluminum. Therefore, $GRAV_{ij}$ in this case would be the gravimetric factor for aluminum in alumina. The gravimetric factor is a well established concept in quantitative chemistry and is defined as the molecular weight of the analyte, Al, divided by the molecular weight of the form it is in, alumina.

$$\frac{2 * MW\_of\_Al}{(2 * MW\_of\_Al + 3 * MW\_of\_O)} = 0.529527$$

Table 10 presents these spike recovery data. Spike recovery data are presented in the final two columns to represent the mean spike recovery and the % variance (based upon 1 σ of triplicate analyses performed on the spiked sample pellet) about that mean. Fluorine was not observed in the spiked sample despite having been reported in Tables 7, 8, and 9. As Table 8 demonstrates, fluorine is not dependably quantified at this level. The values in blue represent those analytes for which spikes were introduced into the sample. Black values are strictly based upon the dilution effect mentioned above.

5. Conclusions

Several conclusions may be observed from the data presented here.

- The Phase 1 sample preparation of cored boards did not provide quality data. This likely had to do with two aspects. First, these boards are heterogeneous. This can be seen in the data variability associated with “replicate” samples cored from different locations on the boards. The second is that the cored boards charred during analysis. Due to this, we were unwilling to perform replicate analyses on any of these Phase 1 samples.

- The Phase 2 efforts to achieve homogeneous samples were successful. Sampling of several aliquots across the circuit boards followed by milling and riffling has achieved reproducible results. This is observed, in particular, in Table 7 where replicate samples were prepared.

- From this it may be inferred that the circuit boards are heterogeneous. The analysis of cored single disks, while the cheaper approach, does not provide dependable data. This was seen in the phase 1 analyses.

- Pellets prepared from these powdered samples are robust and may be used for multiple analyses without significant deterioration.

- The cryo-mill is an appropriate approach to powdering this type of sample. Other mills, hammer and ball mills may also work.

- It is unclear whether the flaked material found after the first milling represents the effect of surface coating or not. It is also possible that it is the result of samples larger than desirable for that size sample container on the cryo-mill

- The pellets prepared by the methods described in this memo were of good quality. However, separation by sieving could have been carried out more extensively and would have ultimately resulted in pellets that were stronger and more homogeneous than those achieved during this work.

- Table 8 describes the short term reproducibility achieved for multiple analyses of a single pellet. The standard deviations described in this table provide one approach to detection limits by this method.

- Table 10 described the recovery of spiked materials. Four elements were deliberately spiked during these experiments. Recovery for these spikes is very good. Copper and calcium, in particular, are excellent at 97 and 103 % recovery. Aluminum and sulfur at 91 and 121 % are also very good recovery. The low recoveries for lead are not considered significant since this element was not spiked and because this element is very close to detection limits. This is seen in Table 8 where %RSD for lead is 30% and the individual analyses are only 6-10ppm.

- The results for chlorine are somewhat unclear. Data for this element shows somewhat more variance than is seen for most other elements. It must be considered possible that some or all of the chlorine represents contamination from the Liquid Binder carrier material, dichloromethane. Two steps, mixing the sample plus binder till it returns to a free flowing state, and operation of the pellet dies under vacuum, were specifically included as quality assurance steps to minimize dichloromethane retention. No proof is available either way. This could be investigated in future work by preparing pellets with both liquid binder and binder pellets. The latter are solvent free.
  However, the Phase 1 chlorine results are also high and variable. No dichloromethane was used in the preparation of these Phase 1 samples.

- When certified standard reference materials are not available for the sample matrix, spiked samples become the best alternative available. This approach is highly dependent upon operator experience and attention to detail. Additional replicates, spiking with other elements would be appropriate for the future.

- The submittal letter described these samples as “halogen free laminates”. This data found one or more halogen in each sample. Chlorine was found in all samples, though the source of that chlorine remains an open question. Separate from chlorine, however, fluorine was found in 1of 7 samples and bromine in 4 of 7 samples. Laboratory contamination does not appear to be a source for either of these elements.

- During the quantification process, matrix of these boards was described as an organic polymeric material. This was used as a “balance compound” during quantification. This was an assumption in the absence of better information. The data can be re-calculated should this be an invalid assumption.

- We have investigated interactions between bromine and arsenic as a result of questions from the committee. As described in a separate section, it is likely that the majority of the arsenic response in the high bromine Phase 1 sample is due to a bromine interference. As described, two corrective approaches are available that could be investigated and implemented in future work.

Appendix A: Responses to Questions

A1. Comments from Draft Version

SS = stainless steel

> Yes. The appropriate section has been edited.

Homogenization and Sub-sampling section. Does “several gram range” refer to 2 to 10 grams?

> Yes, though it is not that specific. The actual capacity is restricted by the mass that can be held in the 2 buckets. That varies with the density of the material.

What is the composition of this binder? Would it have any influence of the results?

> As described in that section, this binder is composed of a polymer dissolved in dichloromethane at a concentration of 100 mg of polymer per 1 mL of solution. The exact composition of the polymer is not provided by the manufacturer, of course; its elemental composition is based upon carbon, hydrogen, oxygen, and nitrogen (per the retailer’s literature).
>
> As an organic structure, the polymer does not have any specific response by XRF; though it may contribute in some small fashion to the baseline. We have found no evidence of elemental contamination from this liquid binder material and it has been used in this laboratory for many years. As described in previous communications, the solvent, dichloromethane, **could** contribute to the chlorine response…if it remained in the pellet until analysis. Our pellet preparation procedures are designed to prevent residual dichloromethane in the prepared pellets.

Are there quality controls associated with this (ZIQ+) analysis? Can you briefly mention what they are?

> On a monthly basis, drift is measured and a correction factor is calculated and stored. This is based upon the analysis of a manufacturer-supplied drift standard.

On a monthly basis, control charts are maintained based upon the analyses of 4 historical standards. These control charts are used to alert personnel to instrumental problems.

For each analysis by this program identification is based upon a manufacturer's supplied library of peaks.

Additional quality control is based upon what the customer specifies. This can include replicate analyses of each pellet or other sample form, analyses of replicate pellets, homogenization procedures, analyses of standard reference materials, when available, and preparation and analysis of spiked samples. For the Phase 2 samples, all of these except standard reference materials were implemented.

Could you express variability as percent coefficient of variation?

This has been done in the pertinent tables.

Could you provide all the raw data for the replicates in an appendix? Printouts of raw data from the computer would be fine. Since the final mean value is a mean of two means, would you agree that expressing the standard deviation or standard error with the means for replicates 1 and 2 would be appropriate?

This raw data will follow separately.

How was the spiking done? Can you add that to the methods section?

A separate experimental section was implemented for this version of the report. The description of the spiking process may be found there.

Why did the wt% of Al not increase with spiking? Ca, S and Cu all increased markedly.

Each additional spiking compound acts as a diluent on the others. As such it is quite possible for a spiked element to be lower on a concentration basis and yet be correct.

Could you provide the gravimetric factors for the analytes so that myself and the partners can understand the calculations? Refers to equation 1

> An expanded description of gravimetric factors has been added above. They may also be found in reference books, such as ***Lange's Handbook of Chemistry***.

Should the %analyte$_i$ be expressed as a percent or as a decimal in this equation? Refers to equation 1

> %analyte should be used in the percent form. This is why there is a factor of 100 in the equation.

Why is spike$_j$ in the denominator, preceded by a sum sign? I see only one value in Table 8 (Now table 5). Refers to equation 1

> The equation includes a Σ because there are 3 spiking compounds added to the sample. J is the counting integer for the multiple spiking compounds and varies from 1-3. The summation is correct. Sample 7+Σ = 2.002, as the final row of Table 5 indicates.

Why is this so high? (Refers to sulfur) I understand variability around 100% but does 119% suggest a measurement problem? Similar for Br and As – 115%

> While sulfur is an element we are "watching," we are not prepared at this time to declare that there is a problem needing resolution with this element. Consider equation 2, where the numerator is based upon experimentally acquired data from the XRF. Similarly, the denominator of 2 comes from equation 1 and also includes experimentally acquired data; both XRF and balance. There is variability in both the numerator and denominator of equation 2 and we would need additional data to be certain biases existed here.
>
> Bromine and arsenic are present at 12 ppm in the unspiked sample. For arsenic, in particular, this must be considered at the detection limit since it was observed in only 1 of 2 replicate samples. At this level for these elements, noise becomes more important and the difference between 100 % and 115 % cannot be considered significant for a single sample.

Conclusions: Could you explain this sentence? The standard deviation describes the detection limits? Doesn't it describe the variability around the mean?

> One definition of detection limit is nσ; where n is an integer selected based upon the desired confidence level. To be done properly, detection limits are measured using dilute samples. In many cases that is shortcut by using the nσ calculation.

Conclusions: Where appropriate, could you provide the detection limits, e.g. for lead?

> As described in the previous response, this depends upon the confidence level desired. N = 3 is generally considered a reasonably conservative approach. Referring to Table 6, short term reproducibility, of the draft report, we can use σ = 0.000237 weight %. 3σ then becomes 0.0007 weight % for lead. This is strictly an estimate that would need to be confirmed experimentally.

Conclusions: Brian et al, could you elaborate your conclusions here … e.g. Brian commented that based on the phase I XRF data, these high chlorine levels may be accurate. Dennis commented that he saw decreasing Cl concentrations as he made replicate measurements

> Simply put, both the range of concentrations and variability are similar between phase 1 and phase 2 samples. Chlorine in phase 1 samples ranged from 0.5 to 0.9 % and had % RSDs ranging from 10 to 40. Similarly, phase 2 samples ranged from 0.4 to 1 % while the % RSD of replicate sample preparations was 25 % for sample 7. And, since no binder was used for the phase 1 samples, there is every indication that the chlorine concentrations observed during phase 1 are real.
>
> Dennis may be referring to the chlorine data where the replicates could be exhibiting a decreasing trend with time. This is, however, a small trend, from 0.92 to 0.81 % across triplicate analysis.
>
> All phase 2 samples exceed the "halogen free" definition for chlorine. Sample 7 is simply consistently high across several sample preparations and analyses.

Conclusions: Yes this is correct – can you explain what a "balance compound" is and how it is used?

In the absence of information about the organic mass present, the material that is not observed by XRF, the quantification program will assign the full sample mass to the analytes observed. This will usually result in unacceptably high, and wrong, results. Informing the program that there is a balance compound present avoids this.

Bromine-Arsenic Question

In an e-mail dated July 15, 2008, [redacted] transmitted a communication from [redacted] regarding a potential interference between bromine and arsenic by XRF. The following figure was prepared by [redacted] from the phase 1 analytical results and was attached to these messages.

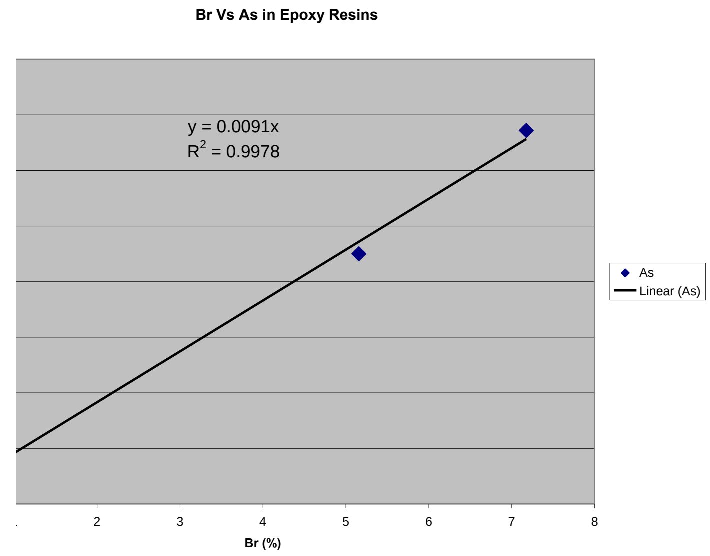


Figure A-1. Bromine vs. Arsenic in Phase 1 samples

This graph clearly shows a direct relationship between the Phase 1 bromine and arsenic results. While there are more than one possible explanation for such a causal relationship, [redacted] warns of a spectral interference leading to arsenic false positives. After investigating the data, there is every indication that he is correct.

The instrument is currently not operational while it awaits the arrival and installation of a new chiller. If the instrument were up, running several known standards would have been the most appropriate approach to investigating this potential interference. Since we do not have that option at the moment, the following several paragraphs consider the question.

Tables A-1 and A-2 provide information on instrumental operational parameters for the several sub-scans and channels that were used for these analyses. “LOCorr” is the acronym for line overlap correction; it is marked yes for the all sub-scans and channels. While the several acronyms used in these tables are not important; what is important is that:

- Channel 2 defines the conditions under which the arsenic data was collected
- Sub-scan 3 defines the conditions under which bromine data was collected
- Channel 2 instrumental conditions match those used under sub-scan 3

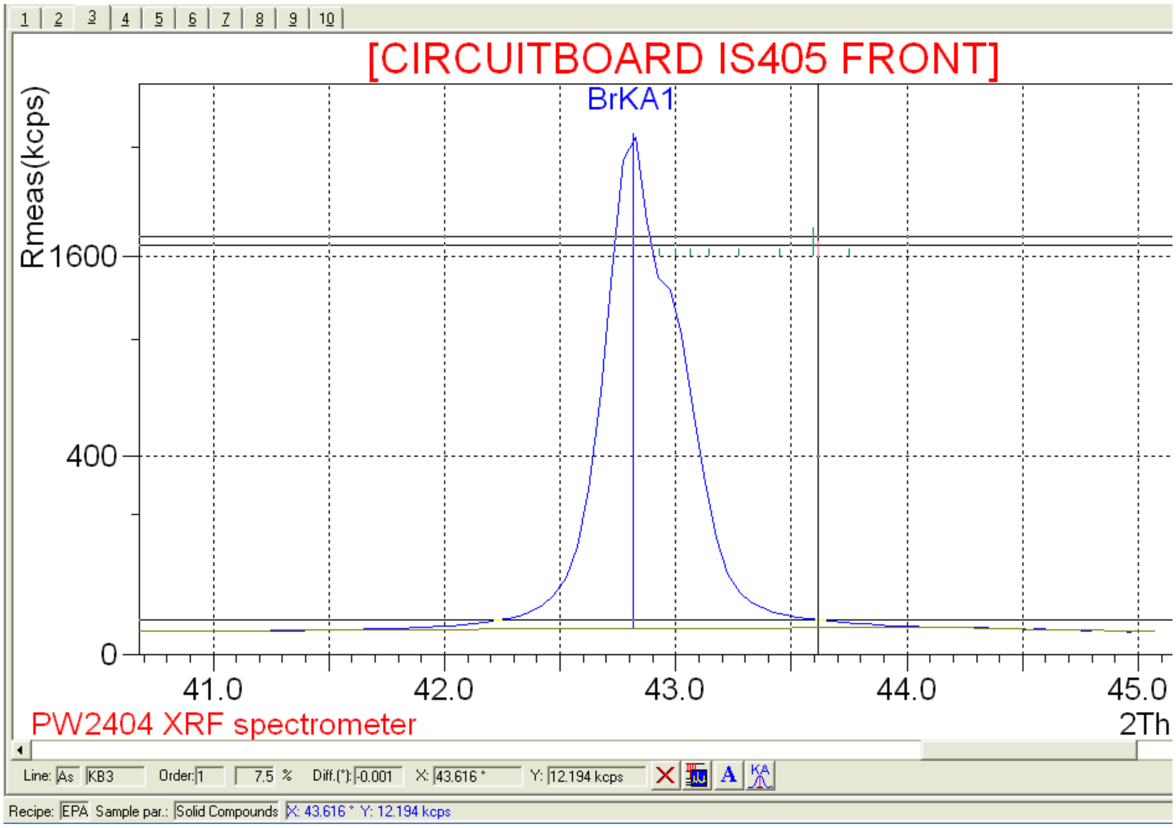
Table A-1. Arsenic and Bromine Scans

Analyte	Line	Scan or channel	Use LOCorr	Measured (kcps)	LO Corrected (kcps)	Used (kcps)	Calculated (kcps)	Difference (kcps)
As	KB	Ch 2	Yes	5.539	5.539	5.532	5.532	0
Br	KB1,3	Sc 3	Yes	542.153	542.153	541.46	541.475	-0.016

Table A-2. Line Selection Parameters

Scan or channel	X-tal	Detector	Collimator (µm)	Tube Filter	kV	mA	Start (°)	End (°)	Step (°)
				material / µm					
Sc 1	LiF220	Scint	150	Brass / 100	60	66	14.02	18.58	0.04
Sc 2	LiF200	Scint	150	Brass / 300	60	66	12.02	20.99	0.03
Sc 3	LiF220	Scint	150	None	60	66	26.63	44.98	0.05
Sc 4	LiF220	Scint	150	Al / 200	60	66	42.03	61.98	0.05
Sc 5	LiF220	Duplex	150	None	50	80	61.03	126	0.05
Sc 6	LiF200	Flow	150	None	32	125	76.04	146	0.08
Sc 7	Ge	Flow	300	None	32	125	91.05	146	0.1
Sc 8	PE	Flow	300	None	32	125	100.1	114.9	0.12
Sc 9	PE	Flow	300	None	32	125	130.1	147	0.12
Sc 10	PX1	Flow	300	None	32	125	20.08	59.98	0.15
Ch 1	LiF220	Scint	150	None	60	66	40.35	40.35	0
Ch 2	LiF220	Scint	150	None	60	66	43.58	43.58	0
Ch 3	LiF220	Scint	150	Al / 200	60	66	45.64	45.64	0
Ch 4	LiF220	Scint	150	Al / 200	60	66	51.65	51.65	0

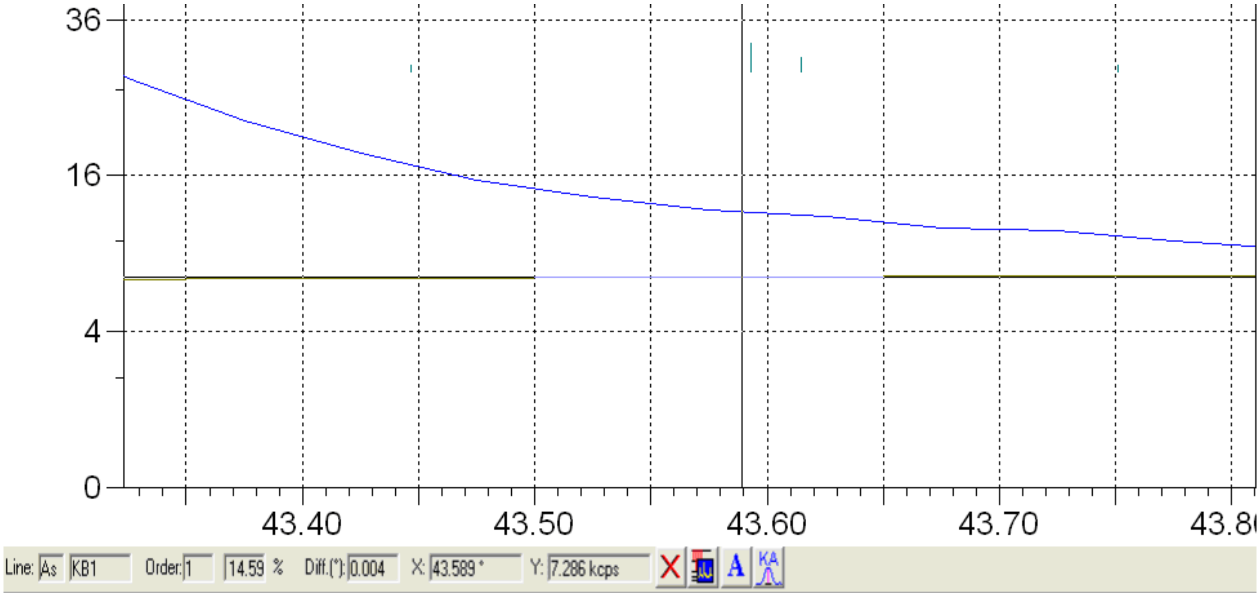
It is, therefore reasonable to examine the sub-scan 3 data for evidence of spectral interference. Figure A-2 provides an expanded view of sub-scan 3 in the vicinity of the arsenic Kβ lines. In Figure A-2, we can observe that the bromine Kα1,2 doublet is in the vicinity of the arsenic Kβ lines. The horizontal colored line below the doublet represents the calculated baseline. The green vertical hashmarks to the right of the doublet represent predicted arsenic peak locations. As can be seen from the cells at lower left, the graphic crosshairs are at the arsenic Kβ3 line and it can be seen that the tail of the bromine doublet contributes a non-zero response at this 2θ angle. Figure A-3 expands the bromine tail region of this spectrum.



Line: As KB3 Order: 1 7.5 % Diff.(°): -0.001 X: 43.616 ° Y: 12.194 kcps

Recipe: EPA Sample par.: Solid Compounds X: 43.616 ° Y: 12.194 kcps

Figure A-2. Sub-scan 3, Bromine doublet



Line: As KB1 Order: 1 14.59 % Diff.(°): 0.004 X: 43.589 ° Y: 7.286 kcps

Figure A-3. Bromine Tail in Arsenic Region

Having said that there is spectral overlap of bromine on arsenic, just as [redacted] noted, we must also note that Table A-2 says that line overlap correction is used. Having said **that**, we must also note that the arsenic response in the LO Corr cell is identical to the measured value, which would seem to contradict that.

Examining Figure A-3 it looks a lot as if the 5.539 kcps measured value in Table A-2 comes from the difference between the calculated background at the crosshair and the bromine tail response. The question remains as to whether or not corrective procedures have been implemented. The ***Panalytical*** software provides 2 approaches to corrective action that are applicable to interferences. One is the already mentioned line overlap correction. The other is a line specific, as opposed to sub-scan specific, background correction procedure. Details on these procedures are not available to the operator within the ***IQ+*** quantification program.

While the details of such applications as ***IQ+Metalloids*** are not available through the ***IQ+*** program, they can be found via the ***Setup*** program. Here we can find that channel 2, arsenic, was set up without any background points. Four are available to provide from 0th to 4th order regressions of curved backgrounds in the vicinity of an analytical channel. By using the channel set button on the bottom of the application specific page, one arrives at a graphic representation of the appropriate standard. On this page, there is a box for defining line overlap interferences. For arsenic in the ***IQ+Metalloids*** application no line overlaps are defined.

In summary, the above suggests there is a strong probability that an uncorrected bromine interference on arsenic exists in this application. Once the instrument is back up, the new chiller is installed, running of standards while modifying the application; followed by re-running certain samples would be appropriate.

There are two comments to be made on this subject

- The applications that are currently on this instrument were set up by the manufacturer’s representative during installation of the software

- As noted in the last few paragraphs, the operator does not have easy access to such details as background correction and line overlap correction.

Appendix B: Laminate Etching and Chlorine Measurements

Both phase 1 and phase 2 samples were sent directly from each manufacturer to David Bedner at ISOLA. Mr. Bedner prepared the laminates for the experiments by etching a portion of the copper from the laminate using standard methods and procedures.

To prepare the copper clad laminates for etching, 33% of the copper was masked with an acrylic tape and 66% of the copper was left exposed. Standard Cupric Chloride solution (2.5% Normal, 130°F) was then applied to the laminate using a Chemcut Etcher model GSK-168 with a line speed of 1.5 feet per minute. Thirty-three percent of each sample's copper surface remained intact after etching. Once etching was complete, the samples were sent to the appropriate laboratory for combustion testing and XRF analysis.

Laminate suppliers certified that the supplied pre-preg samples met the IPC's halogen free definition of less than 900 ppm chlorine (Table B-1). However, the etching process described above caused residual chlorine to be left on the laminates, as demonstrated by a subsequent experiment conducted by ISOLA (Appendix C). As a result, the measured chlorine levels noted in Tables 6 and 7 of the report should be considered in the context of the procedures used to etch the laminates. Furthermore, elemental composition was measured using XRF analysis, which some partners view as less quantitative than other methods. In addition, phase 1 samples were not homogenized prior to analysis, whereas phase 2 samples were homogenized. Dichloromethane was used during homogenization, but specific steps were taken to prevent the samples from retaining any dichloromethane.

Table B-1. Laminate suppliers' independent chlorine analyses

Sample Number	Chlorine concentration in the laminate based upon suppliers analysis by an independent third party
4	**Not provided**
5	**317 ppm** Method : IC
6	**290 ppm** Method: IC
7	**265 ppm** Method: IC

Due to this information, which was discovered after original preparation of the report, DfE would like to alter the tenth conclusion bullet in the report as following (page 15, second bullet):

"The results for chlorine are higher than predicted based on halogen free definitions (<900 ppm chlorine) and are likely due to contamination with chlorine during the etching process when the laminates were prepared. Data for this element also shows somewhat more variance than is seen for most other elements. A second possibility of chlorine contamination was the Liquid Binder carrier material, dichloromethane used for phase 2 sample preparation. Two steps, mixing the sample plus binder till it returns to a free flowing state, and operation of the pellet dies under vacuum, were specifically included as quality assurance steps to minimize dichloromethane retention. Chlorine results for Phase 1 laminates, where no homogenization was done and therefore no dichloromethane was used, are also high and variable. Therefore, chlorine contamination likely came from the etching process. To demonstrate this Mr. Bedner did an experiment comparing chlorine levels of laminates prepared in three different ways. Results are shown in Appendix C."

Appendix C: ISOLA Experiment Demonstrating the Impact of the Etching Process on Chlorine Measurements

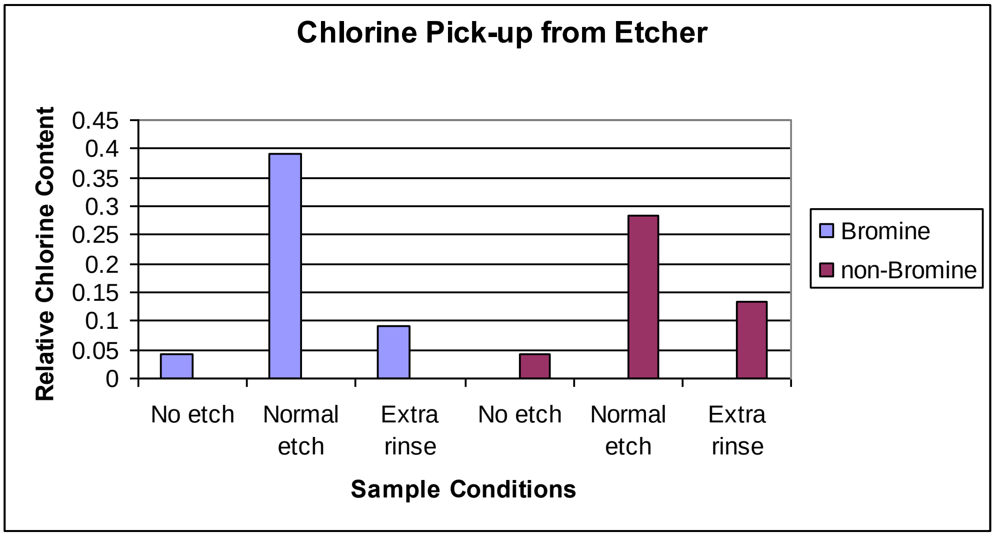
Samples of two laminates, one with a brominated flame retardant and one with a flame retardant that was not brominated, were each prepared one of three ways: 1) copper was peeled from the laminate, i.e. no etching, 2) copper was etched from the laminate using the standard method described in Appendix B or 3) copper was etched from the laminate using the standard method described in Appendix B, followed by an additional de-ionized water rinse before analysis. Chlorine content was analyzed using XRF and results were reported as relative chlorine content compared to known quantity of bromine or another element (proprietary). The results are shown in the Tables and Figures below. Standard etching resulted in 7-9 times more chlorine compared to un-etched laminate whereas additional water rinsing yielded only 2-3 times more chlorine than the un-etched laminate.

Laminate manufacturers typically measure elemental concentrations by IC and believe this is the most accurate method for determining element levels. XRF was chosen for this experiment for the objective of determining general differences in composition between laminate samples, to aid in choosing a diverse set of laminates for Phase II experiments.

XRF measurement

	Br	Cl	X
16533-1	96.85	3.15	
BrFR No Etch	95.98	4.02	
	94.69	5.31	
Average	95.84	4.16	
16533-2	75.20	24.80	
BrFR Normal Etch	71.05	28.95	
	69.30	30.70	
Average	71.85	28.15	
16533-3	95.47	4.53	
BfFR Extra Rinse	89.25	10.75	
	90.31	9.69	
Average	91.68	8.32	
16533-4		2.27	72.57
PFR No Etch		4.63	68.57
		2.13	72.41
Average		3.01	71.18

	Br	Cl	X
16533-5		21.41	56.73
PFR Normal Etch		16.55	61.49
		13.07	62.12
Average		17.01	60.11
16533-6		7.54	59.80
PFR Extra Rinse		7.23	58.63
		8.81	58.51
		7.86	58.98



	Cl pick "normal"	Cl pick up X-Rinse
Bromine Samples	9x	2x
non-Bromine Samples	7x	3x

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX D

U.S. EPA. Flame Retardant in Printed Circuit Boards Partnership: Short Summary of Elemental Analyses. DRAFT. December 9, 2009.

***This Short Summary is based on the work presented in the following three documents, which are also included in Appendix D:**

ICL Industrial. JR 22 – Br and Cl Analysis in Copper Clad Laminates – part II. February 12, 2009. ***(See page A-150)***

ICL-IP Analysis of Laminate Boards. Memo from Stephen Salmon. November 16, 2009. ***(See page A-152)***

Dow. Analysis of Chlorine and Bromine. November 2, 2009. ***(See page A-156)***

Flame Retardant in Printed Circuit Board Partnership

Short Summary of Elemental Analyses

December 9, 2009

Dow and ICL-IP tested the seven laminate samples for elemental composition. Dow tested for bromine and chlorine using neutron activation (NA). ICL-IP tested for aluminum, calcium, magnesium, and phosphorus using ICP, bromine using titration, and chlorine using ion chromatography. Results from Dow and ICL-IP are shown alongside prior XRF results.

Aluminum, Calcium, and Magnesium

The partnership had previously decided to analyze levels of aluminum, calcium, and magnesium to determine whether any of these elements were present as a flame retardant filler, such as $Al(OH)_3$, $Mg(OH)_2$ or $CaCO_3$. As is shown in ICL's report, results for Al, Ca, and Mg were not repeatable. In addition, results were low and further testing showed that Al, Ca, and Mg were not completely digested in the initial procedure. This led ICL to conclude that the Al, Ca, and Mg were most likely from glass fiber or glass treatment, and not from a flame retardant filler (personal communication with ICL, Dec 2009). For these reasons, we do not summarize results for Al, Ca, and Mg here, but instead focus on phosphorus, bromine, and chlorine.

Phosphorus

As is shown in Table 1 and Figure 1, phosphorus levels are highest in laminate 3. There is some discrepancy between XRF and ICP results, but both test methods agree that laminate 3 has the highest level of phosphorus.

Table 1. Phosphorus

	Test Method			
	ICP		XRF	
Laminate	wt%	±[1]	wt%	±[1]
1	0.011	0.0068	0.0016	0.00036
2	0.012	0.0013	0.0017	0.00054
3	1.7	0.020	4.2	0.10
4	1.1	0.054	1.4	n/a
5	0.80	0.0065	0.84	n/a
6	0.69	0.0065	0.74	n/a
7	0.52	0	0.68	0.0049

1: Confidence intervals are based on variance among reported values. It is not possible to determine the extent to which these intervals account for measurement uncertainty.

n/a: not applicable (not enough data to determine confidence bounds)

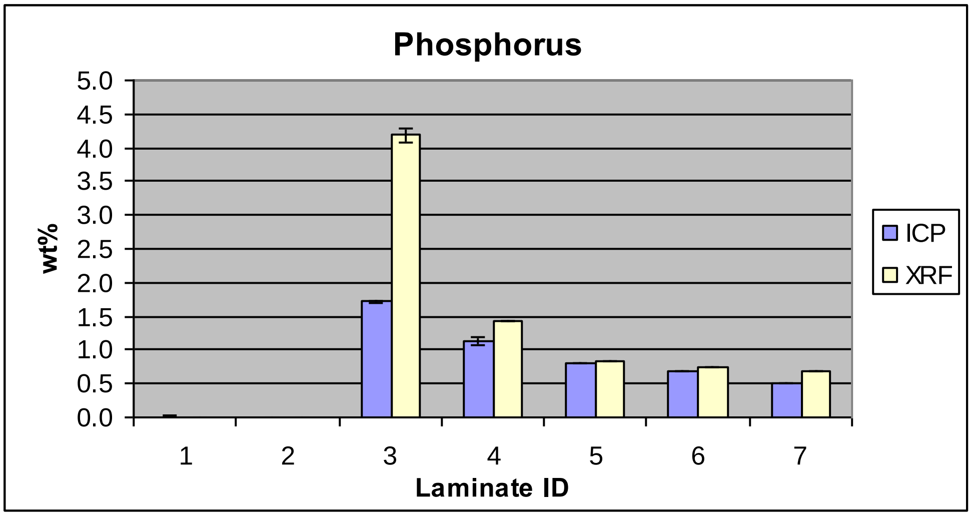


Figure 1. Phosphorus levels measured by ICP and XRF

Bromine

As is shown in Table 2 and Figure 2, bromine levels are highest in laminate 2. There is some discrepancy in results for laminate 1 (titration results are an order of magnitude higher than neutron activation results), but keep in mind that prior testing did not show noticeable levels of brominated dioxins or furans for laminate 1. Laminates 3 through 7 appear to have negligible amounts of bromine (two to three orders of magnitude lower than for laminate 2).

Table 2. Bromine

	Test Method					
	Titration		Neutron Activation		XRF	
Laminate	wt%	±[1]	wt%	±[1]	wt%	±[1]
1	0.7	n/a	0.0017	0.00093	n.d.	n/a
2	8.1	n/a	7.2	0.30	6.1	1.9
3	<0.04	n/a	0.0038	0.000063	0.0047	0.00015
4	<0.04	n/a	0.00054	0.00012	n.d.	n/a
5	<0.04	n/a	0.0026	0.0011	0.0012	n/a
6	<0.04	n/a	0.00011	0.0000098	n.d.	n/a
7	<0.04	n/a	0.0014	0.000079	0.0012	0.00012

1: Confidence intervals are based on variance among reported values. It is not possible to determine the extent to which these intervals account for measurement uncertainty.

n/a: not applicable (not enough data to determine confidence bounds)

n.d.: not detected

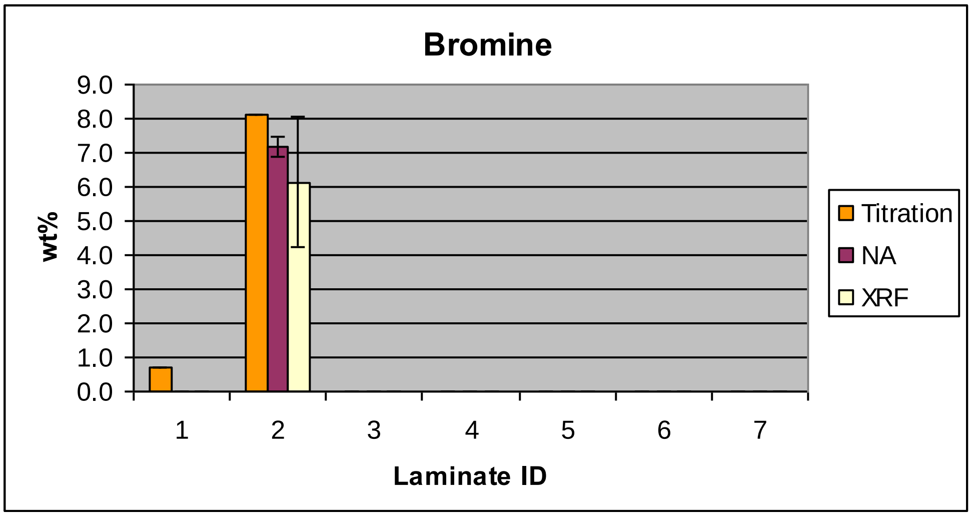


Figure 2. Bromine levels measured by titration, neutron activation (NA), and XRF

Chlorine

Table 3 and Figure 3 show noticeably lower chlorine results with neutron activation and ion chromatography than with XRF (order of magnitude difference), which is as expected under the revised washing protocols. Despite potential discrepancies between test methods, the results show that chlorine levels are similar between laminates, and along the order of 1/100th to 1/10th of a percent by weight.

Table 3. Chlorine

	Test Method					
	Ion Chromatography		Neutron Activation		XRF	
Laminate	wt%	±	wt%	±[1]	wt%	±[1]
1	0.06	n/a	0.075	0.0013	0.88	0.12
2	0.02	n/a	0.073	0.018	0.59	0.35
3	0.02	n/a	0.062	0.0013	0.52	0.081
4	<0.02	n/a	0.063	0.00065	0.45	n/a
5	0.02	n/a	0.060	0.0023	0.43	n/a
6	0.04	n/a	0.046	0.0033	0.49	n/a
7	<0.02	n/a	0.030	0.0020	1.0	0.065

1: Confidence intervals are based on variance among reported values. It is not possible to determine the extent to which these intervals account for measurement uncertainty.

n/a: not applicable (not enough data to determine confidence bounds)

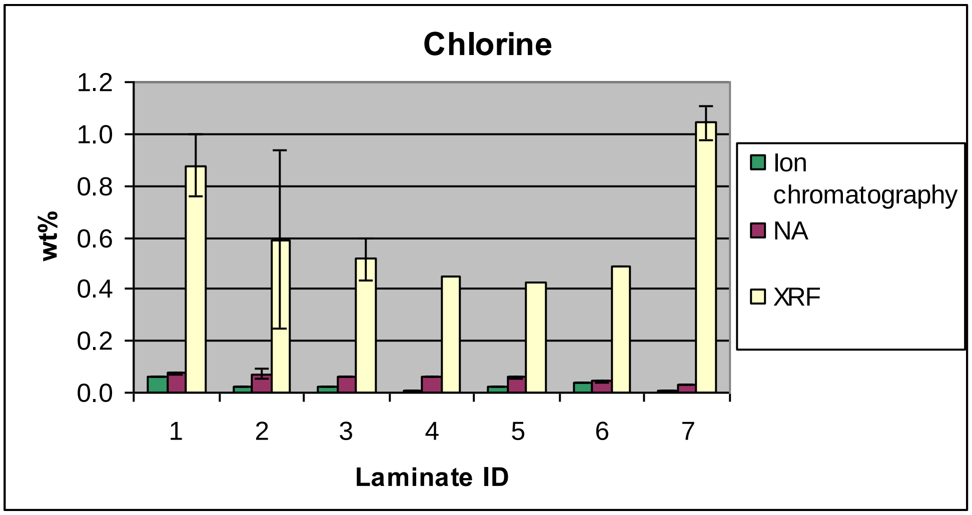


Figure 3. Chlorine levels measured by ion chromatography, neutron activation (NA), and XRF
Note: Ion chromatography results for laminate 4 and 7 were below detection limits, and are shown in Figure 3 as one-half the detection limit.

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Iris Ben-David, Ph.D.

02/12/2009

To: Pierre Georlette

From: Dr. Iris Ben David

Re: JR 2293 – Br and Cl Analysis in Copper Clad Laminates – part II

Following our previous report on the analysis of bromine and chlorine in Copper Clad laminates (see **Appendix-1**) we received a request for analyzing the halides in these samples at levels under 0.5 %. We analyzed the samples using ion chromatography, with detection limit of 0.02 % for chlorine and 0.04 % for bromine.

The results are summarized in the table.

Sample ID	Br Content (%)	Cl Content (%)
EPA-1	0.7 [1]	0.06
EPA-2	8.1 [1]	0.02
EPA-3	< LOD	0.02
EPA-4	< LOD	< LOD
EPA-5	< LOD	0.02
EPA-6	< LOD	0.04
EPA-7	< LOD	< LOD

Notes:

1) Determined by titration – see **Appendix-1**.

Please let us know if you need any additional analyses for these samples.

With Best Regards,

Iris Ben David

Appendix-1: Our report from November 11, 2009 – JR 2283.

11/11/2009

To: Pierre Georlette

From: Dr. Iris Ben David

Re: JR 2283 – Br & Cl Analysis in Copper Clad Laminates

We received seven samples of Copper Clad laminates (marked EPA-1 to EPA-7). We analyzed the samples for their bromine and chlorine contents. Two of the samples had metal strips on them; we examined only the metal free section, in comparison with the other samples.

The Br/Cl contents are given below:

Sample ID	Br Content	Cl Content
EPA-1	0.7 % (± 0.4 %)[1]	n.d.[2]
EPA-2	8.1 %[3] (± 0.2 %)[4]	n.d.
EPA-3	n.d.	< 0.5 %[4]
EPA-4	n.d.	< 0.5 %
EPA-5	n.d.	< 0.5 %
EPA-6	n.d.	< 0.5 %
EPA-7	n.d.	< 0.5 %

Notes:

2) The uncertainty at 1 % level is 5 %.
3) n.d. = Not detected.
4) Average of 5 specimens (including the second set of samples EPA 2).
5) The uncertainty at 10 % level is 2 %.

The analytical method used has a limit of quantification of 0.5 %. At levels under 0.5 % the uncertainty is >50%. If the accuracy at lower levels of halides is important and should be determined, we can use a different analytical method. Upon request, the analytical results will be available within a month.

With Best Regards,

Date: November 16, 2009

Subject: Analysis of Laminate Boards.

From: Stephen Salmon, ICL-IP

Determination of P, Al, Ca, Mg

Analyses were completed on seven laminate boards. The results show repeatability was very good for P, but very poor for Al, Ca, and to a lesser extent Mg. The nature of the sample matrix appears to be the problem. Details are given below.

The laminate boards were sampled by taking very thin slices across areas that did not contain any of the copper cladding. The slivers were cross cut to produce very small pieces. This material was mixed and sub-sampled for acid digestion to get a representative sample across the board. It was noted that this cutting procedure produced some very fine glass dust from the edges of the pieces. Some of this dust was included in the sub-samples.

The samples were digested with sulfuric acid using nitric acid and 30% hydrogen peroxide as needed to destroy the organic matrix. The resulting solution contained the insoluble fiberglass. The digested samples were filtered through 0.45 um polypropylene syringe filters into 100-mL volumetric flasks and made to volume at 4% sulfuric acid. The samples prepared in triplicate were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) using calibration standards matched to the 4% sulfuric acid of the samples.

Results for triplicate analyses of the seven laminate boards are shown in Table 1.

Table 1
ICP Analysis of slivered laminate boards

Sample ID	wt% Al	wt% Ca	wt % P	wt% Mg
EPA-1 A	0.21	0.54	0.017	<0.01
EPA-1 B	0.26	0.62	<0.01	0.010
EPA-1 C	0.19	0.45	0.010	<0.01
EPA-2 A	0.31	0.78	0.011	0.013
EPA-2 B	0.32	0.79	0.011	0.013
EPA-2 C	0.39	0.93	0.013	0.016
EPA-3 A	0.21	0.50	1.71	<0.01
EPA-3 B	0.40	0.32	1.71	<0.01
EPA-3 C	0.48	0.78	1.74	<0.01
EPA-4 A	0.35	0.68	1.14	0.080
EPA-4 B	1.60	3.34	1.07	0.14
EPA-4 C	0.27	0.74	1.16	0.070
EPA-5 A	1.09	0.69	0.80	0.014
EPA-5 B	2.34	0.51	0.81	0.013
EPA-5 C	0.34	0.26	0.80	<0.01
EPA-6 A	2.67	1.63	0.68	0.056
EPA-6 B	2.96	1.37	0.69	0.046
EPA-6 C	2.21	0.72	0.69	0.040
EPA-7 A	2.86	1.74	0.52	0.085
EPA-7 B	3.09	2.14	0.52	0.10
EPA-7 C	1.81	0.96	0.52	0.059

The results show that only P determination was repeatable. To check if the fine glass dust that was included at various levels in the acid digested samples skewed the results four of the laminate boards were prepared again in triplicate. This time a single chip of sample of the desired weight was cut out of three sections of the laminate board. The acid digestion and ICP-OES analyses were repeated.

The results of this evaluation are shown in Table 2.

Table 2
Repeat Digestions on single laminate board chips.

Sample ID	wt% Al	wt% Ca	wt % P	wt% Mg
EPA-4 A chip	0.31	0.66	1.18	0.070
EPA-4 B chip	0.22	0.72	1.23	0.068
EPA-4 C chip	0.23	0.73	1.23	0.073
EPA-5 A chip	0.38	0.25	0.81	0.004
EPA-5 B chip	0.80	0.67	0.83	0.010
EPA-5 C chip	0.85	0.57	0.83	0.011
EPA-6 A chip	2.91	1.35	0.63	0.043
EPA-6 B chip	0.77	0.85	0.70	0.018
EPA-6 C chip	1.87	1.29	0.69	0.024
EPA-7 A chip	0.49	0.24	0.50	0.017
EPA-7 B chip	0.39	0.34	0.51	0.016
EPA-7 C chip	0.43	0.35	0.51	0.012

The results show that P again was very repeatable and matched the values from digestion of the small pieces. Al and Ca, and to a lesser extent Mg, again showed very poor repeatability.

The acid digestion of the single chip samples resulted in four small sheets of fiberglass from each sample. These were recovered from the filtration step and the washed fiberglass was dried and weighed. The fiberglass was subjected to the acid digestion procedure again and an ICP-OES analysis showed significant and variable amounts of Al and Ca had not been recovered by the first digestion. Mg showed the same to a lesser extent, but P was not detected indicating quantitative recovery in the original digestion.

Table 3 shows the results of this evaluation.

Table 3
Redigestion of fiberglass recovered from digestion of single chips.

Sample ID	wt% Al	wt% Ca	wt % P	wt% Mg
EPA-6 A chip 2nd	0.45	0.50	nd	0.016
EPA-6 B chip 2nd	0.64	1.30	nd	0.030
EPA 6 C chip 2nd	0.41	0.086	nd	0.011

The conclusion is that Al and Ca are in the fiberglass or can not be separated from the sample matrix quantitatively. This is also the case for Mg, but to a lesser extent. P, however, is quantitatively recovered from the laminate board matrix by the procedure used.

Determination of Br and Cl

An analysis of slivered laminate board for halogens was attempted by metallic sodium reflux in isopropanol with silver nitrate titration for Br and Cl. Unfortunately, the laminate board matrix proved to be impervious to extraction by the reagent and this approach had to be abandoned.

Samples of the seven laminate boards were sent to ICL in Israel for sample preparation by sodium peroxide bomb. Preliminary results are shown below. Other results are pending and will be sent when available.

Date: 11/11/2009
To: Pierre Georlette
From: Dr. Iris Ben David

Re: JR 2283 – Br & Cl Analysis in Copper Clad Laminates

We received seven samples of Copper Clad laminates (marked EPA-1 to EPA-7). We analyzed the samples for their bromine and chlorine contents. Two of the samples had metal strips on them; we examined only the metal free section, in comparison with the other samples.
The Br/Cl contents are given below:

Sample ID	Br Content	Cl Content
EPA-1	0.7 % (± 0.4 %)[1]	n.d[2]
EPA-2	8.1 %[3] (± 0.2 %)[4]	n.d.
EPA-3	n.d.	< 0.5 %[4]
EPA-4	n.d.	< 0.5 %
EPA-5	n.d.	< 0.5 %
EPA-6	n.d.	< 0.5 %
EPA-7	n.d.	< 0.5 %

Notes:
1) The uncertainty at 1 % level is 5 %.
2) n.d. = Not detected.
3) Average of 5 specimens (including the second set of samples EPA 2)
4) The uncertainty at 10 % level is 2 %.

The analytical method used has a limit of quantification of 0.5 %. At levels under 0.5 % the uncertainty is >50%. A different analytical method will be used to get more precise Cl results. The analytical results will be available within two weeks.

Triplicate samples were prepared by transferring 0.3 grams respectively into pre-cleaned 0.25-dram polyethylene vials. Samples were measured for thickness and cleaned with isopropanol prior to placing into the vials. Areas with copper were not sampled. Standards of chlorine, bromine were prepared from standard solutions and placed into pre-cleaned 0.25 dram vials. The standards were diluted to the same volume as the samples and the vials heat-sealed. The samples, standards and blanks were irradiated and counted in four batches. Triplicate samples of EPA -2 were irradiated separately using 0.01grams. The higher concentration of bromine identified interferes with the detection of chlorine. Thickness was measured in triplicate using a micrometer.

Sample ID	20 min @ 250 kW		10 min @250 kW		10 min @30 kW 10 min decay	
	Cl (ppm) t_d =1 h = 1 h	Br (ppm) t_d =1 h t_c = 1 h	Cl (ppm) t_d =1 h t_c = 1 h	Br (ppm) t_d =1 h t_c = 1 h	Cl (ppm) t_d =1 h t_c = 1 h	Br (ppm)
EPA 1	760±40	15.5±0.8	740±40	9.7±0.5	740±40	25.9±1.3
EPA 3	630±30	38.2±1.9	630±30	37.8±1.9	610±30	37.1±1.9
EPA 4	640±30	4.5±0.2	630±30	5.2±0.3	630±30	6.5±0.3
EPA 5	600±30	20.6±1.0	580±30	37.8±1.9	620±30	20.1±1.0
EPA 6	440±20	1.0±0.1	440±20	1.1±0.1	490±20	ND@2ppm
EPA 7	290±10	13.3±0.7	320±20	14.7±0.7	290±10	14.0±0.7

10 min@5kw: Cl t_d =10 min, t_c = 7 min; Br t_d = 5 hour, t_c = 1.5 hour						
Sample ID	Cl (ppm)	Br (wt%)	Cl (ppm)	Br (wt%)	Cl (ppm)	Br (wt%)
EPA 2	650±130	6.9±0.3	920±180	7.4 ±0.4	630±130	7.3±0.4

Thickness	Inch	Inch	Inch	Average± Stdev
EPA 1	0.018	0.021	0.019	0.019±0.002
EPA 2	0.016	0.018	0.018	0.018±0.001
EPA 3	0.019	0.019	0.02	0.020±0.001
EPA 4	0.018	0.017	0.02	0.019±0.001
EPA 5	0.018	0.018	0.018	0.018±0.001
EPA 6	0.017	0.017	0.017	0.017±0.001
EPA 7	0.018	0.018	0.018	0.018±0.001

FLAME RETARDANTS IN PRINTED CIRCUIT BOARDS: APPENDIX E

University of Dayton Research Institute. Use of Cone Calorimeter to Identify Selected Polyhalogenated Dibenzo-P-Dioxins/Furans and Polyaromatic Hydrocarbon Emissions from the Combustion of Circuit Board Laminates. October 22, 2013.

USE OF CONE CALORIMETER TO IDENTIFY SELECTED POLYHALOGENATED DIBENZO-P-DIOXINS/FURANS AND POLYAROMATIC HYDROCARBON EMISSIONS FROM THE COMBUSTION OF CIRCUIT BOARD LAMINATES

Final Report
Prepared for the U.S. Environmental Protection Agency

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Research Triangle Park, NC 27711

October 22, 2013

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LIST OF ACRONYMS

1556 HFR	1556 halogen-free flame retardant
ASTM	American Society for Testing and Materials
Avg HRR	Average heat release rate
BFR	Brominated flame retardant
CIL	Cambridge Isotope Laboratories
CO/CO_2	Carbon monoxide/carbon dioxide
DfE	Design for the Environment Program
DQI	Data quantity indicator
DQO	Data quantity objective
EMPC	Estimated maximum possible concentration
EMT	Environmental Monitoring Technologies Inc
EPA	U.S. Environmental Protection Agency
E-waste	Electronic waste
FIGRA	Fire growth rate
FMS	Fluid Management Systems Inc
FTT	Fire testing technology
GC/MS	Gas chromatography/mass spectrometry
HFR	Halogen-free flame retardant
HRGC	High resolution gas chromatography
HRMS	High resolution mass spectrometry
HRR	Heat release rate
ISO	International Organization for Standardization
KOH	Potassium hydroxide
LRMS	Low resolution mass spectrometry
MARHE	Maximum average rate of heat emission
NFR	No flame retardant
NGO	Non-governmental organization
NRMRL	National Risk Management Research Laboratory
OSL	EPA Organic Support Laboratory
P	Populated by halogen components
PAHs	Polyaromatic hydrocarbons
PBDD/Fs	Polybrominated dibenzo-p-dioxins/furans
PCB	Printed circuit board
PCDD/Fs	Polychlorinated dibenzo-p-dioxins/furans
Peak HRR	Peak heat release rate
PFK	Perfluorokerosene
PHF	Populated by low-halogen components
PM	Particulate matter
PUF	Polyurethane foam
R&D	Research and development
RoHS	Restriction of Hazardous Substances
RTP	EPA Research Triangle Park
TBBPA	Tetrabromobisphenol A
TEF	Toxic equivalent factor
TEQ	Toxic equivalent quantity

THR	Total heat release
Tig	Time to ignition
UDRI	University of Dayton Research Institute
UL	Underwriters Laboratories
UV	Ultraviolet
WEEE	Waste Electrical and Electronic Equipment

1 Executive Summary

The U.S. Environmental Protection Agency (EPA) Design for the Environment (DfE) program convened a partnership to conduct an alternatives assessment for TBBPA in printed circuit boards. The partnership determined that combustion testing of sample laminates using the alternatives would strengthen the assessment and industry decision-making on use of alternatives. This report explains the outcome of that testing.

The purpose of this study was to understand the potential emissions of halogenated dioxins or furans and polyaromatic hydrocarbons (PAHs) from burning circuit board laminates. The methods of this study mimic two types of fire events: open burn and incineration of electronic waste (e-waste), both of which are used for precious metal recovery. While difficult to model these two complex fire scenarios exactly, the University of Dayton Research Institute (UDRI) utilized a cone calorimeter, a fire safety engineering instrument capable of simulating these scenarios and measuring combustion efficiency.

Combustion conditions, as well as model samples for burning, were selected with input from a group of stakeholders "Partnership" assembled by DfE. These stakeholders included circuit board laminate manufacturers, flame retardant producers, government regulators, and non-governmental organizations (NGOs) with vested interests in the potential emissions from these burning items. Some stakeholders funded the UDRI experiments while EPA funded the sample extractions and dioxin/furan analyses.

The results of this study show that when these materials are burned, even at high heat flux that would attempt to mimic an incinerator, various pollutants are released. Further, flame retarded materials release more PAHs and other pollutants when burning compared to materials that are not flame retarded, but this is expected and indicates that the flame retardants are working as designed. Specifically, the retardation of flame and combustion will result in more incomplete combustion products.

The combined dioxin/furan and PAH emission studies suggest that circuit board polymers cannot be analyzed in isolation when determining emissions; the entire populated board must be considered. While certain pollutants were found in both flame retardant and non-flame retardant circuit boards, toxicity studies were not conducted. Therefore the relative toxicity of the combustion by-products from the different laminate formulations can only be partially calculated.

While the exact flame retardants used in this study were not identified to the Partnership, the flame retardant chemistry of these materials behaved as expected. Brominated flame retardants inhibited combustion and produced brominated phenols (detected, but not quantified), dioxins, furans, and other aromatics during burning. Non-halogenated flame retardants (presumed to be phosphorus-based) slowed down burning through char formation. This generated more PAHs than the non-flame retardant circuit boards in certain circumstances (lower heat flux) but less PAHs when compared to BFRs.

In general, these emissions fit the known combustion chemistry of these flame retardants classes. Therefore, this study contributes data supporting the approach that, to achieve both fire safety and lower emissions, disposal must be done properly with full incineration and appropriate air pollution control devices in place.

Despite this confirmation of open burning pollution, the study does also leave some questions unanswered. The results from this study are not definitive regarding which specific pollutants were released since chemical identification was limited. Further, the results do not show which chemistries and circuit board components may lead to lower emissions, even under simulated incineration conditions. A cone calorimeter may not achieve temperatures as high as those of real-world incinerators. The high heat flux results may not be fully indicative of real-world emissions should printed circuit boards be put into an incinerator. Because some flame retardants (including those in this report) inhibit combustion even at very high heat fluxes, additional research is needed to identify circuit board flame retardant chemistry with lower environmental and human health impact emissions. Incinerator conditions are likely to reduce the emissions, but additional emission controls (baghouses, filters) may be needed to prevent all emissions of concerns as the efficiency of an incinerator is a function of its design and actual operation temperatures.

Finally, this study demonstrated that the technique of using the cone calorimeter (ASTM E1354) for emission studies in combination with a custom-built emissions capture sampling train was successful with small samples. Specifically, the cone calorimeter can be used to collect emissions from circuit board materials without having to conduct actual open burns. However this proved to be a labor intensive analytical technique needing refinement of procedures. To summarize the findings of this study:

50 kW/m^2 heat flux:
- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at higher levels than NFR sample.
- NFR: PAHs emitted at lowest levels compared to other samples.

100 kW/m^2 heat flux:
- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at lowest levels compared to other samples.
- NFR: PAHs emitted at a level slightly lower than the BFR sample.

Effect of components on emissions:
- PBDD/Fs: PBDD/Fs were similar or lower than sample without components.
- PAHs: In general, presence of components reduced PAH emissions for BFR, were similar or slightly higher for HFR and were lower for 1556 HFR. The size of these differences varied depending on how PAHs were defined (see section 4.6).

Smoke, PM, CO and CO_2 release:
- Smoke release was higher for BFR than HFR laminates. Smoke release was higher with components due to greater amount of material. PM generally had small differences between samples. There were negligible differences in CO release between samples. CO_2 release was lowest for BFR but with small differences between samples. Results are complex and smoke/PM results do not always correlate.

2 Introduction

2.1 Electronic Waste

According to statistics gathered by the Electronics TakeBack Coalition, which were derived from EPA statistics, 2.4 million tons of e-waste were generated in 2010, only 27% of which was recycled (see Table 2-1).[1] However, with the price of precious metals and rare earths increasing due to demand and geopolitical issues, there is increased demand to recycle electronics in order to recover the metals and rare earths. One of the more popular and cost-effective techniques for this type of metal/rare earth recovery is incineration, which burns off the polymeric components of the e-waste and leaves behind inorganic ash. This ash can be further smelted down and refined to isolate the precious metals and rare earths. When incineration is not conducted properly, the combustion of polymeric components creates toxic by-products that can be released into the environment. Improper incineration of electronics in developing countries, as seen in popular magazines like National Geographic[2], has led to concerns about the improper disposal of these products and has influenced the research in this report. Improper disposal of waste that leads to widespread environmental damage and under-ventilated toxic by-product release is highly undesirable and illegal in many countries. This issue may be attributable to companies sending e-waste to countries with looser regulations for improper incineration instead of following incineration regulatory standards in place in many developed countries. The drivers for improper waste disposal are numerous, but ultimately financial, and the drive to recover precious metals is causing more developed countries to keep the wastes inside borders to recycle materials via internal infrastructure. However, even for operations that will utilize clean burning incinerators and afterburner/scrubber technology, there still needs to be some knowledge of what is being released from burning this waste so incinerators can be designed and engineered correctly.

Table 2-1. E-Waste by Category in 2010

E-Waste by Ton in 2010				
Products	**Total disposed** (tons)**	**Trashed (tons)**	**Recycled (tons)**	**Recycling Rate (%)**
Computers	423,000	255,000	168,000	40%
Monitors	595,000	401,000	194,000	33%
Hard copy devices	290,000	193,000	97,000	33%
Keyboards and Mice	67,800	61,400	6,460	10%
Televisions	1,040	864,000	181,000	17%
Mobile devices	19,500	17,200	2,240	11%
TV peripherals*	Not included	Not included	Not included	Not included
Total (tons)	2,440,000	1,790,000	649,000	27%
E-Waste by Unit in 2010				
Products	**Total disposed** (units)**	**Trashed (units)**	**Recycled (units)**	**Recycling Rate (%)**
Computers	51,900,000	31,300,000	20,600,000	40%
Monitors	35,800,000	24,100,000	11,700,000	33%
Hard copy devices	33,600,000	22,400,000	11,200,000	33%
Keyboards and Mice	82,200,000	74,400,000	7,830,000	10%
Televisions	28,500,000	23,600,000	4,940,000	17%
Mobile devices	152,000,000	135,000,000	17,400,000	11%
TV peripherals*	Not included	Not included	Not included	Not included
Total (units)	384,000,000	310,000,000	73,700,000	19%

Computer products include CPUs, desktops, and portables.
Hard copy devices are printers, digital copiers, multi-functions and faxes.
Mobile devices are cell phones, personal digital assistants (PDAs), smartphones, and pagers.
*Study did not include a large category or e-waste: TV peripherals, such as VCRs, DVD players, DVRs, cable/satellite receivers, converter boxes, game consoles.
**"Disposed" means going into trash or recycling. There totals don't include products that are no longer used, but which are still stored in homes and offices.

[1] Table adapted from "Facts and Figure on E-Waste and Recycling", Electronics TakeBack Coalition, 2012. Statistics from "Electronics Waste Management in the United States Through 2009", U.S. EPA, 2011.

2.2 Performance Requirements for Printed Circuit Boards

The materials in printed circuit boards are influenced by performance and regulatory requirements that must be met by manufacturers. These selections ultimately influence the emissions from these components when they burn. For electronic products produced today, numerous environmental requirements must be met. Environmental regulations in the European Union, namely the Restriction of Hazardous Substances (RoHS)[3] and Waste Electrical and Electronic Equipment (WEEE)[4] directives have been driving the elimination of specific metals and organic compounds of environmental concern so that incineration and recycling are easier, and in the event of improper disposal, environmental damage is limited. Regulations from one nation automatically affect other nations as most electronics manufacturers prefer to produce for a global market rather than tailor specific products for specific markets that would result in higher manufacturing and research and development (R&D) costs.

Flame retardants are added to consumer products, including printed circuit boards, to protect highly flammable polymers against potential fire/ignition risks. The primary fire risk that flame retardants are protecting against in circuit boards is that of an electrical fault or short circuit ignition source that can cause the polymer (typically an epoxy) to thermally decompose and ignite. This ignition site can lead to flame spread across the board and can cause the electronic casing (also typically made out of flammable polymer) to also ignite, which may lead to flame spread out of the electronic device into a larger compartment such as a home, a vehicle, or a mass transport structure (e.g., subway, train, bus), which may contain other flammable products that can cause the initial fire to further propagate. If a fire gets out of control, one might hypothesize that because flame retardants may prevent a product from being fully consumed in an accidental fire event, there is less total emissions when compared to a non-flame retardant product that fully ignites. This is especially true if the non-flame retardant product is composed of a high heat release material which in turn causes other nearby objects to burn and lead to a large fire event (flashover). It should be pointed out though that this toxic emission reduction enabled by flame retardant products in the event of accidental fires is only realized in life cycle models if that product is disposed of properly at the end of its lifetime.[5,6,7] If products are not disposed of properly then flame retardants have some potential to leach into the environment and lead to measureable levels of pollution. The flame retardant technology in use today for most circuit boards typically consists of brominated bisphenol A epoxies that are co-polymerized into the circuit board, or are reactive phosphorus-based flame retardants that are also co-polymerized into the circuit board.[8,9,10] These technologies have been in use for decades because they are cost-effective and reliable while not compromising other essential epoxy circuit board properties (e.g., electrical insulation properties, mechanical). These systems in place today served as the baseline for the DfE project initially conducted in 2008-09 to study the emissions of circuit boards using brominated and phosphorus-based flame retardants.[11]

2.3 Project Goal

The goal of this project was to understand the potential emissions of halogenated dioxins, halogenated furans, and PAHs and fire characteristics of a standard tetrabromobisphenol A (TBBPA) laminate compared to different halogen-free laminates in various scenarios with and without typical circuit board components. The methods of this study mimic two types of fire events used for precious metal recovery: open burning and proper incineration. Definitions of open burning and proper incineration are needed here:

- Open burning means that combustion is done in a crude vessel, open to the environment, where there are no good engineering measures in place to capture emissions or drive the combustion process to completion.
- Proper incineration means that combustion is carried out in a system designed and engineered to fully combust a material can capture its emissions through the use of afterburner and baghouse-type emissions capture systems.

The results will provide scientific information to aid electronics and electrical manufacturers in their decision-making processes to design and choose sustainable and environmentally-friendly materials for their products.

3 Experimental Methods

A series of circuit boards were selected based on Phase I of this project to be tested under various conditions mimicking open burning and incineration operations. The components used on circuit boards were ground up and combusted along with the copper-clad circuit board laminate to simulate the potential emissions from printed circuit board e-waste. An overview of the testing methodology for Phase II of this project is provided in Table 3-1.

Table 3-1. Overview of Phase II Testing Methodology

Laminates Burned (Acronym)	TBBPA laminate (BFR) Non-flame retardant laminate (NFR) Halogen-free flame retardant laminate (HFR) Halogen-free flame retardant laminate (1556-HFR)
Components Burned	Standard halogen components (P) Low-halogen components (PHF)
Laminate/Component Combinations Burned	BFR + standard halogen components (BFR +P) BFR + low-halogen components (BFR + PHF) HFR + standard halogen components (HFR + P) HFR + low-halogen components (HFR + PHF) 1556-HFR + standard halogen components (1556HFR + P) 1556-HFR + low-halogen components (1556HFR + PHF)
Scenarios (Heat Flux)	Open Burn (50 kW/m^2) (Laminate Name -50) Incineration (100 kW/m^2) (Laminate Name – 100)
Analytes Tested	Polybrominated dibenzo-p-dioxins/furans (PBDD/Fs) Polyaromatic hydrocarbons (PAHs)

Multiple entities were responsible for conducting different parts of Phase II's combustion testing experiment. Figure 3-1 depicts the workflow throughout the project. DfE facilitated and oversaw the workflow by communicating directly with Isola, Seagate, UDRI, and EPA Research Triangle Park (RTP).

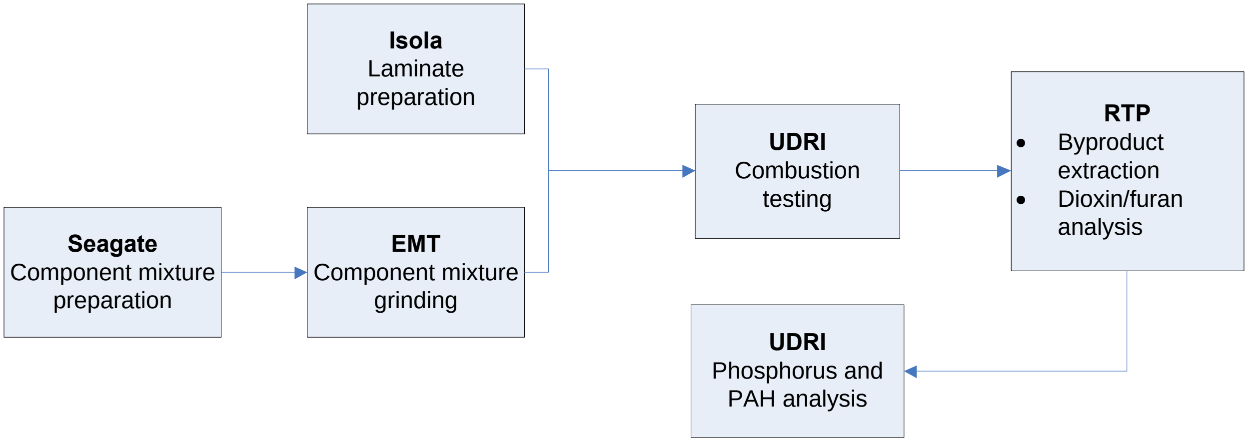

Figure 3-1. Overview of Workflow for Combustion Testing and Analysis

The circuit board laminates selected and the conditions used to burn the components and circuit board combinations are shown in Table 3-2. This experimental plan was created with input from the DfE stakeholders participating in this project including government officials, NGOs, circuit board laminate manufacturers, electronics producers, and flame retardant producers. The instrument and method selected to mimic open burning and incineration was the cone calorimeter, which is a standard fire science measurement tool (ASTM E1354, ISO 5660) used to quantify heat release, smoke release, and CO/CO$_2$ emissions from burning objects in a variety of fire scenarios. This tool was chosen based on UDRI hypothesis that it could mimic burning conditions of interest to the program while providing quantitative emissions on complex heterogeneous circuit board samples. More specifically, the cone calorimeter provided a dynamic model in that it could burn a realistic amount of material (an actual circuit board laminate with components or component mimics) and be instrumented in such a way to capture all of the emissions from that burning event.

UDRI and EPA conducted the experiments in Table 3-2 in 2011. The original experiment plan included a third combustion scenario for low-oxygen combustion. These low-oxygen experiments were not carried out because the low-oxygen attachment for the cone calorimeter was unable to yield dependable results for simulated smelting conditions at 100 kW/m^2 heat flux at 10% O_2. The investigators discovered that when a sample was initially pyrolyzed/burned under these conditions, combustion gases escaped from the top of the unit where they could potentially be exposed to more oxygen. This event could lead to a more complete combustion and thus generate inaccurate results. For reasons of integrity and efficiency, UDRI and the partnership collectively decided to exclude the 100 kW/m^2 heat flux at 10% O_2 test condition from the study.

Table 3-2. Emission/Combustion Tests for Phase II DfE Work

Heat flux	Combustion atmosphere	Sample description	# of blank runs[1]	# of laminate burns	PBDD/Fs	Test Blanks for PBDD/Fs	PAHs	Phosphorus
50 kW/m^2	Air (Open-burn)	BFR	2	2	x	x	X	x
		BFR + P	2	2			X	x
		BFR + PHF	2	2	x	x	X	x
		HFR	1	2			X	x
		HFR + P	1	2		x	X	x
		HFR + PHF	1	2			X	x
		1556 HFR	1	2			X	x
		1556 HFR + P	1	2		x	X	x
		1556 HFR + PHF	1	2			X	x
		NFR	1	2			X	x
100 kW/m^2	Air (Incineration)	NFR	1	2		x	X	x
		BFR	1	2	x	x	X	x
		HFR	1	2			X	x
		Subtotal	***16***	***26***				
		Total (blanks + laminates)	***42***					

[1] Blanks between burns of the same laminate for the first several burns that could produce PBDD/Fs were analyzed for PBDD/Fs carry-over. The blanks were clean; therefore the number of blanks in subsequent sets of samples was reduced.

3.1 Laminate Preparation

The laminate manufacturer Isola was responsible for laminate preparation. Each laminate was 61cm x 46cm (2,806cm^2) and had a 4-ply 2116 Taiwan glass S409 finish. These samples were prepared by pressing each side of the laminates with 1oz of shiny copper from Nan Ya and etching a portion of the copper from the laminate using standard methods and procedures, just as was done during Phase I testing (see Phase 1 Report)[12], followed by a rinse with dilute KOH. To prepare the copper clad laminates for etching, a portion of the copper was masked with an acrylic tape and the rest of the copper was left exposed. Standard cupric chloride solution (2.5% normal, 266°C) was then applied to the laminate using a chemical etching machine. Etched laminates were then washed with KOH (2.5% normal) to remove residual chlorine. During preliminary testing, laminates were washed only with water and not with KOH. However, it is standard practice in industry to wash laminates with dilute KOH after etching, so the partnership decided to replicate this approach to reflect real-world conditions.

Due to a miscommunication, Isola initially etched off 25% of the copper, leaving 75% of the surface area covered by copper. However, the partnership agreed that a copper surface area of approximately 33% would be more representative of real-world conditions. The copper was distributed evenly over the surface in a way that allowed UDRI to cut the laminate into 100mm x 100mm squares for combustion testing, each containing an equal amount of copper. In order to achieve a surface area as close as possible to 33% and also obtain an even distribution of copper, Isola etched the copper so that 25% remained on one side, and 37.5% on the other side. This resulted in total surface area coverage of 31%. The total amount of copper present in the actual samples is shown in Table 3-3. Pictures of representative samples of the four different copper clad sample types are provided in Figure 3-2 through Figure 3-5.

Table 3-3. Copper Area of Circuit Board Laminates

Sample Description-Heat Flux (kW/m^2)	Copper area content (%)
BFR - 50	32.01
BFR - 50	32.56
BFR - 100	32.95
BFR - 100	32.85
BFR + P - 50	33.86
BFR + P - 50	33.50
BFR + PHF - 50	32.85
BFR + PHF - 50	32.76
HFR - 50	32.66
HFR - 50	32.78
HFR - 100	32.72
HFR - 100	32.68
HFR + P - 50	32.98
HFR + P - 50	32.65
HFR + PHF - 50	32.96
HFR + PHF - 50	31.90
1556 HFR - 50	32.92
1556 HFR - 50	32.86
1556 HFR + P - 50	33.12
1556 HFR + P - 50	33.10
1556 HFR + PHF - 50	32.87
1556 HFR + PHF - 50	32.68
NFR - 50	32.75

Sample Description-Heat Flux (kW/m^2)	Copper area content (%)
NFR - 50	32.80
NFR - 100	32.22
NFR - 100	32.25

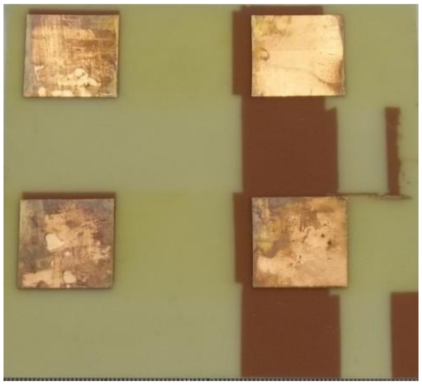

Figure 3-2. NFR Sample

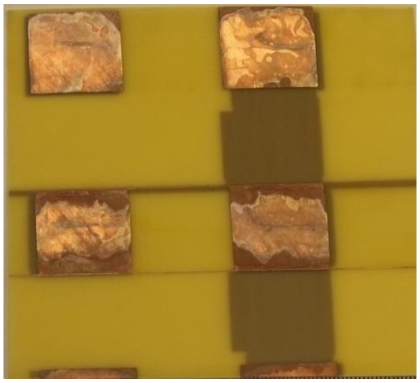

Figure 3-3. BFR Sample

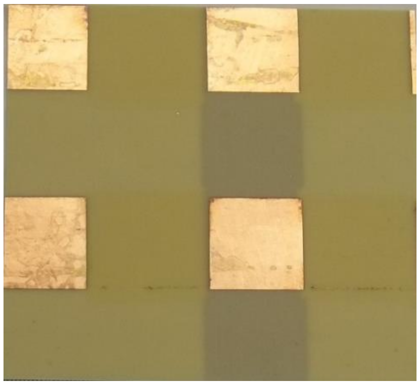

Figure 3-4. HFR Sample

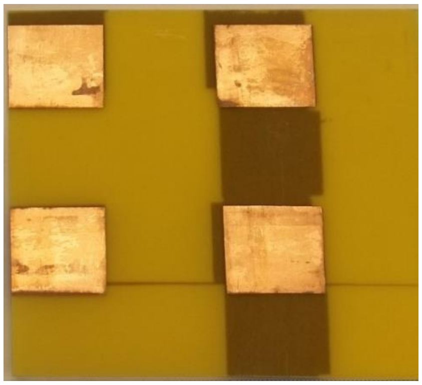

Figure 3-5. 1556-HFR Sample

3.2 Component Mixture Preparation and Component Mixture Grinding

Seagate prepared a standard mixture of components, which Environmental Monitoring Technologies, Inc. (EMT) ground up and sent to UDRI for combustion testing. The mixture was combusted with selected laminate samples to simulate populated circuit boards. Both a low-halogen mixture and a standard halogen mixture were prepared and were added to the laminates. To the extent possible, the types of components in the low-halogen and standard halogen mixtures were made identical. Seagate formulated and supplied the mixtures based on the electronic components found on standard disk drive boards. Seagate provided as much detail as possible about the composition of the ground-up mixtures and calculated the amount to add to each laminate sample. The mixtures included integrated circuits, resistors, capacitors, connectors (main source of plastic housing), shock sensors, and accelerometers. The partnership decided to grind up components into a mixture prior to combustion testing. The blend of components that was ground up to mimic circuit board components is shown in Table 3-4. Since the chemical composition of the component mixtures will determine emissions, Seagate provided information on the chemicals present in the component mixtures, which is shown in Appendix C: Elemental Analyses of Component Mixtures.

There are a few advantages to using ground-up components instead of whole components:

- More reliable results: Combustion results are consistent for ground-up components, but are not consistent for whole components. This is because small changes in the placement of whole components on the boards can affect the amount and type of materials that come into contact with each other during combustion, which affects the formation of combustion by-products.
- Better estimate of worst-case-scenario: Using ground-up components ensures maximum contact between component materials and would give a higher probability of producing combustion by-products.
- More inclusive sample: Capacitors can be included in the mixture of ground-up components, as they are not an explosion hazard when ground-up.
- Less variability in sample preparation: Components do not have to be attached to the laminate, which removes potential sources of variability (e.g., human error that might occur while fixing components to the laminate and increased probability of introducing contaminants).

Table 3-4. Blend of Components to Mimic Circuit Board Components

Component	Amount (g)	
	Typical PCB[1]	**Component Mix**
Resistor (fixed)	0.07	30.77
Capacitor	1.59	694.51
Shock Sensor	0.03	10.94
Xstr (thermistor, bipolar transistor, FET)	0.08	33.19
Frequency Drive	0.06	25.38
EMIRFI Filter	0.02	6.57
Inductor	0.53	229.82
Integrated Circuit (custom drive specific, linear, memory)	1.64	718.82
Connector	3.05	1335.17
Total	7.05	3085.17

[1] Typical circuit board component mass/surface area of board is 0.128 g/cm^2. The component mixture loading used for experiments was 0.1 g/cm^2 (10±0.05 g/100 cm^2 of laminate burned).

3.3 Combustion Testing

3.3.1 Cone Calorimeter Apparatus Description

A cone calorimeter (FTT, United Kingdom) housed at UDRI was modified and used to characterize emissions from combustion of various printed circuit board laminate samples. The cone calorimeter is a fire testing instrument which quantitatively measures the inherent flammability of material through the use of oxygen consumption calorimetry, and is a standard technique[14] under ASTM E-1354/ISO 5660. This instrument was designed primarily as a fire safety engineering tool, but has found great utility as a scientific tool for understanding fire performance in relation to regulatory pass/fail tests as will be referred to in the next paragraph. In effect, it mimics a well-ventilated forced combustion scenario of an object being exposed to a constant heat source and constant ventilation (Figure 3-6). This scenario represents many real world fires where an object or material is aflame and radiates heat to other objects that also catch fire as a result. The cone calorimeter serves as a very useful fire safety engineering tool by looking at the heat release rates of a material under these forced conditions.

By studying the various parameters measured by the cone calorimeter, one can correlate the cone calorimeter measurements to other tests, or, bring understanding of how a material behaves when a flame is exposed to various fire scenarios. Work on comparing cone calorimeter to other tests has included full scale flammability tests,[15] bench scale tests like UL-94 or limiting oxygen index,[16-20] automotive material flame spread tests,[21] wire and cable flame spread tests,[22] and other types of fire tests/scenarios[23-26]. A schematic of the cone calorimeter basic setup is shown in Figure 3-6.

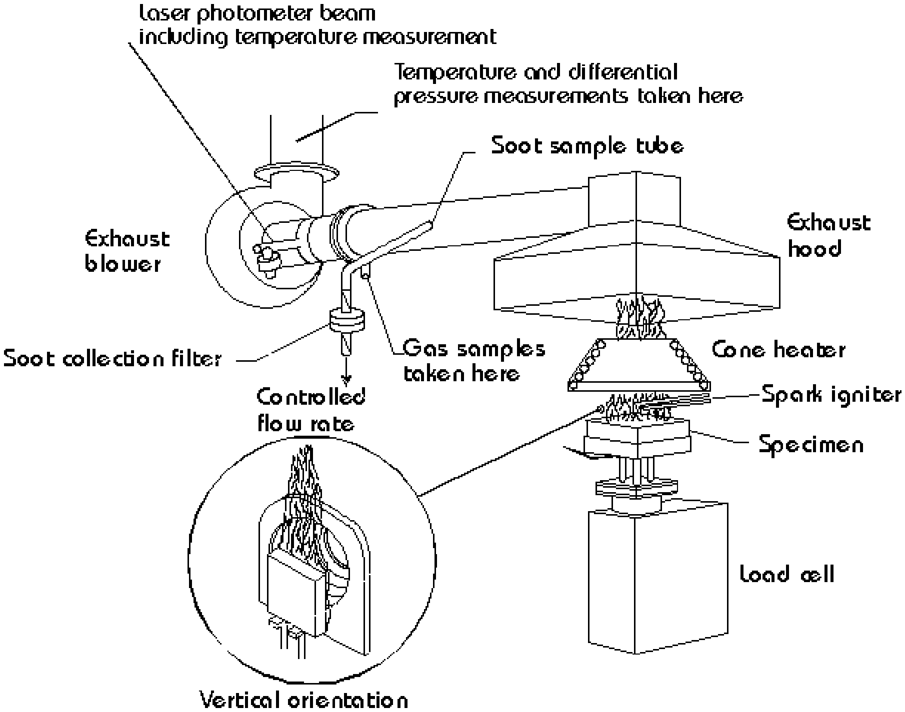

Figure 3-6. Cone Calorimeter Schematic

Several measurements can be obtained from the cone calorimeter. The cone calorimeter at UDRI is equipped with a laser for smoke measurements (laser photometer beam in Figure 3-6), oxygen sensor (paramagnetic) for measuring oxygen consumption, and load cell for measuring mass loss as the sample pyrolyzes during heat exposure. The instrument at UDRI also has a CO/CO_2 (infrared-based) detection system, allowing for the measurement of CO/CO_2 production as a function of time during sample combustion. From these parts of the instrument, various measurements are collected during each test which can reveal scientific information about material flammability performance. These include:

- Time to ignition (Tig): Measured in seconds, this is the time to sustained ignition of the sample. Interpretation of this measurement assumes that earlier times to ignition mean that the sample is easier to ignite under a particular heat flux.
- Heat Release Rate (HRR): The rate of heat release, in units of kW/m^2, as measured by oxygen consumption calorimetry.
- Peak Heat Release Rate (Peak HRR): The maximum value of the heat release rate during the combustion of the sample. The higher the peak HRR, the more likely that flame will self-propagate on the sample in the absence of an external flame or ignition source. Also, the higher the peak HRR, the more likely that the burning object can cause nearby objects to ignite.
- Time to Peak HRR: The time to maximum heat release rate. This value roughly correlates the time it takes for a material to reach its peak heat output, which would in turn sustain flame propagation or lead to additional flame spread. Delays in time to peak HRR are inferred to mean that flame spread will be slower in that particular sample, and earlier time to peak HRR is inferred to mean that the flame spread will be rapid across the sample surface once it has ignited.
- Time to Peak HRR – Time to Ignition (Time to Peak HRR – Tig): This is the time in seconds that it takes for the peak HRR to occur after ignition rather than at the start of the test (the previous measurement). This can be meaningful in understanding how fast the sample reaches its maximum energy release after ignition, which can suggest how fast the fire grows if the sample itself catches fire.
- Average Heat Release Rate (Avg HRR): The average value of heat release rate over the entire heat release rate curve for the material during combustion of the sample.
- Starting Mass, Total Mass Lost, Weight % Lost: These measurements are taken from the load cell of the cone calorimeter at the beginning and end of the experiment to see how much total material from the sample was pyrolyzed/burned away during the experiment.
- Total Heat Release (THR): This is measured in units of MJ/m^2 and is the area under the heat release rate curve, from time to ignition to time to flameout, representing the total heat released from the sample during burning. The higher the THR, the higher the energy content of the tested sample. THR can be correlated roughly to the fuel load of a material in a fire, and is often affected by polymer chemical structure.
- Total Smoke Release: This is the total amount of smoke generated by the sample during burning in the cone calorimeter from time to ignition to time to flameout. The higher the value, the more smoke generated either due to incomplete combustion of the sample, or due to polymer chemical structure. Note that this is a light obscuration measurement, and the smoke measurement does not discriminate between particulate matter (PM) which obscures light and organic vapors/pyrolyzed molecules which also may obscure light.
- Maximum Average Rate of Heat Emission (MARHE): This is a fire safety engineering parameter,[27] and is the maximum value of the average rate of heat emission, which is defined as the cumulative heat release (THR) from time t=0 to t divided by time t. The MARHE can best be thought of as an ignition modified rate of heat emission parameter, which can be useful to rank materials in terms of ability to support flame spread to other objects.
- Fire Growth Rate (FIGRA): This is another fire safety engineering parameter, determined by dividing the peak HRR by the time to peak HRR, giving units of kW/m^2 per second. The FIGRA represents the rate of fire growth for a material once exposed to heat, and higher FIGRA suggest faster flame spread and possible ignition of nearby objects.

- CO/CO_2 Yields: This is the total measured amounts of CO/CO_2 measured during testing, pre-ignition and post-ignition. The yields are in units of kg gas (CO, CO_2) per kg sample.

3.3.2 Cone Calorimeter Testing Methods

Circuit board samples were provided as very thin (0.4mm to 0.6mm thick) epoxy + e-glass laminates. These laminates contained copper plating in squares on both sides of the laminates and were cut in such a way that each sample had the same amount of copper metal present in the same configuration. Since the laminates provided were too large to be tested as is in the cone calorimeter, the samples were cut into 100 cm^2 square ($\pm 0.1cm^2$) pieces for cone calorimeter testing. Samples were not conditioned in any way prior to testing. All of the samples were tested as single ply laminates, with some of the laminates also having ground component powder put upon them in 10g batches prior to testing in the cone. Any powder used was weighed out right before the cone experiment and spread evenly across the sample surface. The powder was not conditioned before use but was always kept in a sealed jar and was weighed out with a typical benchtop digital scale (accurate to +/- 10mg).

Samples tested included epoxy with brominated flame retardant (BFR), epoxy with non-flame retardant (NFR), and two epoxies each with different halogen-free flame retardant additives (HFR). Powders put on the board samples include standard halogen-containing component powder (P) and low halogen-containing component powder (PHF).

Cone calorimeter experiments were conducted on a FTT Dual Cone Calorimeter as per the ASTM E-1354-07 method at two heat fluxes (50 kW/m^2 and 100 kW/m^2). Samples were tested in triplicate without frame and grid, with the back side of each sample wrapped in aluminum foil. The only deviation from the ASTM method was that an exhaust flow of 15 L/s was used instead of the standard 24 L/s exhaust flow rate. The lower flow rate was used to better mimic the “open burning” fire scenario as the normal 24 L/s flow rate would give more oxygen to the fire than is typically seen in a “open burning” flaming combustion scenario. Heat release rate data from cone calorimeter can be found in Appendix A: Circuit Board Flammability Data.

3.3.3 Sampling Train

The total sampling train was designed and constructed specifically for these experiments to collect the total exhaust gas emitted from the combustion of samples in a standard cone calorimeter (Figure 3-7 and Figure 3-8). Sampling the total exhaust reduces the amount of sample that has to be burned to characterize and quantify emissions. The exhaust duct on the FTT Dual Cone Calorimeter from Fire Testing Technology Limited, UK, was modified to enable connecting of the total sampling train. The exhaust hood above the combustion zone was connected to the sampling exhaust duct (110mm in diameter) with a cooling jacket (not used for these experiments). The sampling exhaust duct was connected to a stainless steel filter holder 61cm x 25.5cm x 2.5cm. The filter holder holds three 20.5cm x 25.5cm filters. The filter holder was connected to an amber-glass coiled-condenser to cool the hot gas flowing before it entered an amber-glass cartridge containing four polyurethane foam (PUF) cartridges of 10cm x 5cm meant to capture semi-volatile organic compounds. Amber glass is important to note here since many of the chemical species of interest in this study can be UV light sensitive. The PUFs were retained by a fritted Teflon disk inside the cartridge. The gas exiting the PUFs was passed through an impinger which was connected to a vacuum pump and the gas exiting the pump was directed to the cone calorimeter exhaust system through a wire reinforced vacuum tube.

At the beginning of each sampling period after assembling the sampling train, the system was checked for leaks. Once any leaks were fixed, the air flow was set to 15 L/s by turning the vacuum pump on and using a gate valve to control the air flow. All the circuit board laminate samples tested were exposed to a heat flux of 50 kW/m^2 or 100 kW/m^2. For additional details on the cone heater temperature (which is not the temperature that the samples encountered during burning), see Appendix B: Experimental Conditions. Once the cone reached its set temperature, the cone calorimeter ignition was turned on and samples were placed in the sample holder at the center of the cone heater and ignited. Once the samples ignited, they were allowed to burn until no flame and smoke were detectable. During sampling, the gas temperature inside the sampling train was constantly monitored at eight different positions. The first two thermocouples (T1 and T2) were placed inside the stainless steel duct at 5cm and 25.5cm from the exhaust hood above the cone to monitor the gas temperature entering the duct (T1) and entering the filter holder (T2). The third thermocouple (T3) was placed at the outlet of the filter holder (or entrance of condenser). The fourth thermocouple (T4) was positioned at the inlet of the PUF cartridge and the fifth thermocouple (T5) was placed to monitor the gas temperature exiting the PUF cartridge. The cold bath temperatures are adjusted to maintain the PUF cartridge exit gas temperatures (T5) to ~20-25°C. However, the average gas temperatures exiting the PUFs were ~30°C for all experiments. The other thermocouples were used to monitor the water bath temperatures for the stainless steel duct water jacket, the condenser, and the glass cartridge water jacket. All thermocouples used were 3mm sheath diameter, grounded, type K thermocouple probes from Omega Engineering, Stamford, Connecticut. During sampling, the pressure dropped inside the sampling train and the flow through the sampling train was constantly monitored by a digital gauge manometer placed at the pump inlet and by a differential flow meter on the cone calorimeter exhaust system, respectively. When the soot particles started to build up on the glass filter and decreased the gas flowing through it, the flow was adjusted by opening the gate valve situated at the inlet of the pump.

Post-sampling, the sampling train was disassembled; the condensate from the condenser was recovered to a pre-cleaned container for analysis, the various components of the train were covered with hexane-rinsed aluminum foil and transported to the recovery lab. In the recovery lab, the filters and PUFs were removed, the filters were weighed to determine their PM loading and the entire sampling train (from the hood and duct work above the cone/combustion zone) up to the inlet of the impinger was rinsed with three solvents (methanol, methylene chloride and toluene, respectively) to recover condensed material for analysis. All solvent rinses, condensate, PUFs and filters were stored in pre-cleaned amber glass containers with Teflon lined caps; the solvent levels were marked with the appropriate labels; and were refrigerated till they were either shipped to the analytical lab or were analyzed at UDRI using GC/MS. The glass fiber filter and PUF adsorbents were shipped to the Organic Support Laboratory (OSL) of EPA at RTP where they were combined together, extracted, and analyzed for PxDD/Fs. After extraction, the OSL of EPA at RTP shipped back a part of the PUF and Filter extract to UDRI to analyze for PAHs and phosphorous-containing compounds. The analytical methods used to quantify involved isotope dilution and internal standard procedures that are described later in Sections 3.6 through 3.8. After the final solvent rinse (i.e., toluene), the metal duct and filter holder were rinsed with methylene chloride and covered with hexane-rinsed aluminum foil until the next experiment; the glassware was rinsed with Sparkleen soap solution/deionized water and baked at 475°C for 8 hours in a Barnstead Thermolyne Pyro-clean Trace oven for baking glassware. After baking, the glassware was rinsed with methylene chloride and covered with hexane-rinsed aluminum foil. A field blank was performed to check for carry over and memory effects.

All fluorescent lights in the laboratory, as well as in the fume hood, were covered with clear UV-absorbing filters supplied by UV Process Supply, Chicago, Illinois. This was done to minimize/eliminate decomposition of UV light sensitive compounds from the pre-sampling surrogates and samples recovered from the experiments. The three solvents used were toluene (Envisolv, 34413) and Methanol (Pestanal, 34485) purchased from Sigma-Aldrich, Milwaukee, Wisconsin and Methylene Chloride (Pestisolv, PS 724) purchased from Spectrum Chemicals, New Brunswick, New Jersey at purity levels required as per EPA method 23 for analysis of dioxins and furans. The 150 mm glass-microfiber filters (TE-EPM2000) without binder were purchased from Whatman, USA. The PUFs were purchased from Tisch Environmental. The PUFs and the filters were cleaned by the OSL at EPA, RTP by Soxhlet extraction with methylene chloride for 16 hours and wrapped in aluminum foil, labeled, and shipped to UDRI in airtight cans to use for sampling.

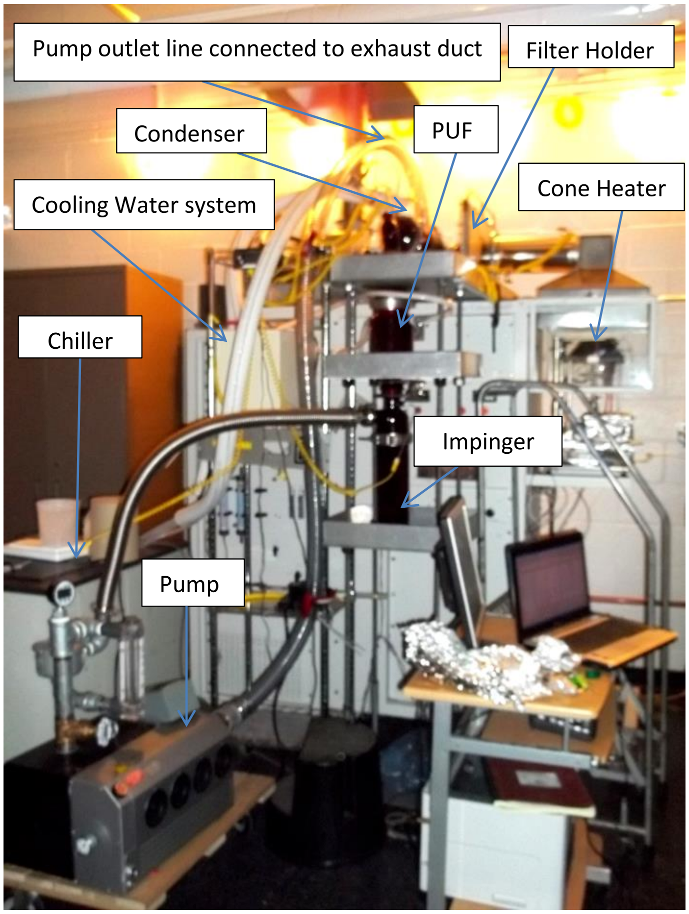

Figure 3-7. Total Sampling Train Coupled with UDRI Cone Calorimeter

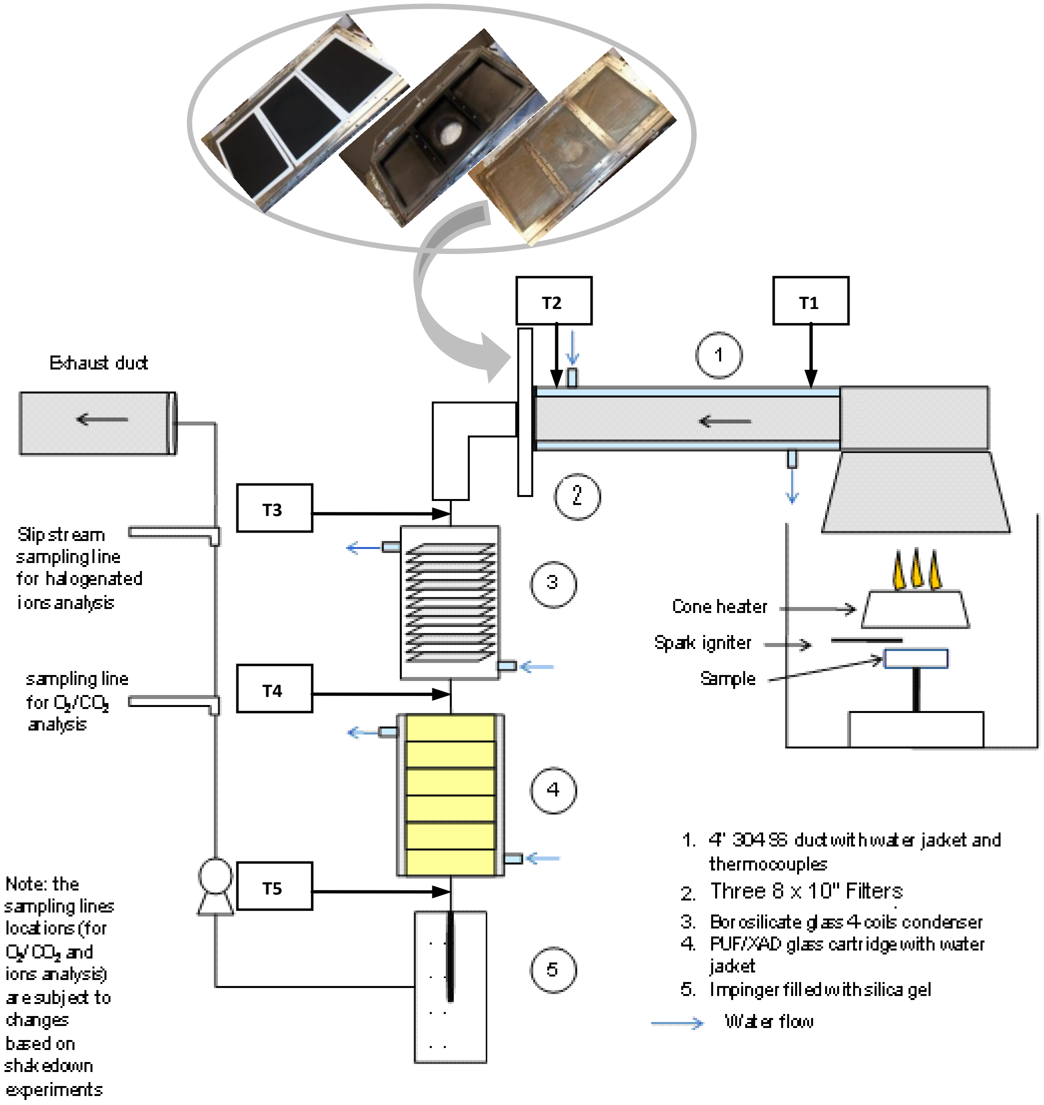

Figure 3-8. Schematic of Total Sampling Train

Prior to taking the sampling train from the sample prep/recovery lab to the cone test facility, the cleaned PUFs were placed in the glass cartridge and spiked with the necessary pre-sampling surrogates, the filters were weighed and placed in the filter holder and the glass cartridge and filter holder were sealed with hexane-rinsed aluminum foil and transported to the cone calorimeter laboratory with all other glassware and components also wrapped in hexane-rinsed aluminum foil. The printed circuit board laminate samples to be tested were also weighed and placed in a hexane-rinsed aluminum foil sample holder and were covered with hexane-rinsed aluminum foil.

3.3.4 Samples Tested

To ensure that enough material could be detected, especially in the case of small quantity compounds of interest (specific dioxins and PAHs), minimum levels of laminate and components had to be tested; they were cut into 100cm^2 square pieces. Four types of laminates were tested for Phase II: laminate without flame retardant (NFR), laminate containing brominated flame retardant (BFR), laminate containing halogen-free flame retardant (HFR), and laminate containing halogen-free flame retardant (1556-HFR). The printed circuit board laminate samples were tested at two different heat fluxes to mimic different combustion scenarios. The lower heat flux (50 kW/m^2) was used to mimic an "open burn" type of event and the higher heat flux (100 kW/m^2) was used to mimic an incinerator furnace condition that would be encountered during incineration of the boards.

3.4 Sample Handling and Custody

3.4.1 Shipping Custody

Samples were collected at UDRI, packaged, and shipped by UPS to RTP. In RTP, the samples were received and brought to the laboratory and then opened by the laboratory custodian. The samples were stored in laboratory refrigerators until extraction. The sample custody form was included in the shipping cooler, and the UPS records are the custody records for the transfer from UDRI to RTP. The boxes and coolers were sealed with tape and the tape was removed in the laboratory.

3.4.2 Sample Identification and Log

Each sample was given an identifying laboratory code number and name (laboratory ID). The laboratory ID was assigned to the samples upon receiving and samples were logged in the sample ID log book along with the sample name and project description. The code sequence was explained to the laboratory personnel to prevent sample mislabeling. Proper application of the code simplified sample tracking throughout the handling, analysis, and reporting processes. Table 3-5 shows the laboratory ID coding that was used in this study. PUF and Filters were not given separate numbers.

Table 3-5 Laboratory ID Coding System

YYMMXX

Laboratory ID Code	Sample Type
YYMM	Year and month of the sample logging in the laboratory system
XX	Consecutive sample number of the given year (YY) and month (MM)

3.5 By-product Extraction

After the samples were collected and shipped back to RTP, the EPA OSL performed extraction, cleanup, and fractionation of samples provided by UDRI. The extracts were analyzed using High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) for target PCDD/Fs and PBDD/Fs (Table 3-6). The results were reported in a spreadsheet to UDRI for inclusion in the final report (results were reported as amounts per sampling train). In very early samples, less than ten percent of the dioxins and furans were found in the sampler rinses and the rinses would cause very high shipping costs, so only the PUF and filters from each sample were sent to RTP for extraction and analysis.

3.5.1 Organic Compound Target List

Chlorinated and brominated dioxins and furans (PCDD/Fs and PBDD/Fs, respectively) were targeted in this project. Analysis concerned 2,3,7,8-substituted congeners of PCDD/Fs (17 congeners) and their brominated counterparts (only 13 2,3,7,8 PBDD/Fs congeners were reported due to limited availability of commercial standards). Table 3-6 presents the congener-specific list of PCDD/Fs and PBDD/Fs target analytes.

Table 3-6. PCDD/Fs and PBDD/Fs Target Analytes

Congener Pattern	PCDD/Fs targets	PBDD/Fs targets
2,3,7,8	TeCDD	TeBDD
1,2,3,7,8	PCDD*	PBDD
1,2,3,4,7,8	HxCDD	HxBDD
1,2,3,6,7,8	HxCDD	HxBDD
1,2,3,7,8,9	HxCDD	HxBDD
1,2,3,4,6,7,8	HpCDD	HpBDD
1,2,3,4,6,7,8,9	OCDD	OBDD
2,3,7,8	TeCDF	TeBDF
2,4,6,8	***	TeBDF**
1,2,3,7,8	PCDF	PBDF
2,3,4,7,8	PCDF	PBDF
1,2,3,4,7,8	HxCDF	HxBDF
1,2,3,6,7,8	HxCDF	***
1,2,3,7,8,9	HxCDF*	***
2,3,4,6,7,8	HxCDF*	***
1,2,3,4,6,7,8	HpCDF	HpBDF
1,2,3,4,7,8,9	HpCDF	***
1,2,3,4,6,7,8,9	OCDF	OBDF

* Were reported as co-elution.

** FromTeBDF homolog group 2,4,6,8 -TeBDF can be reported because it was present in the calibration solution and therefore has an accurate retention time.

*** In the various calibration solutions, 18 different congener patterns were included, e.g. 2,3,7,8. Of the 18 individual congener patterns that were looked for, five were only in one of the solutions (either bromo or chloro).

3.5.2 EPA-RTP Experimental Strategy

Figure 3-9 presents the original experimental strategy for RTP’s part of the project. The first phase of this project was extraction, cleanup and fractionation (described in detail in Section 3.5.3 and Section 3.5.4 of this report) of samples provided by UDRI for HRGC/HRMS instrumental analysis of PCDD/Fs and PBDD/Fs. The second phase described in detail in Section 3.6.2 was the instrumental analysis. The third phase of the analysis was data processing and reporting (see Section 3.6.3 for details).

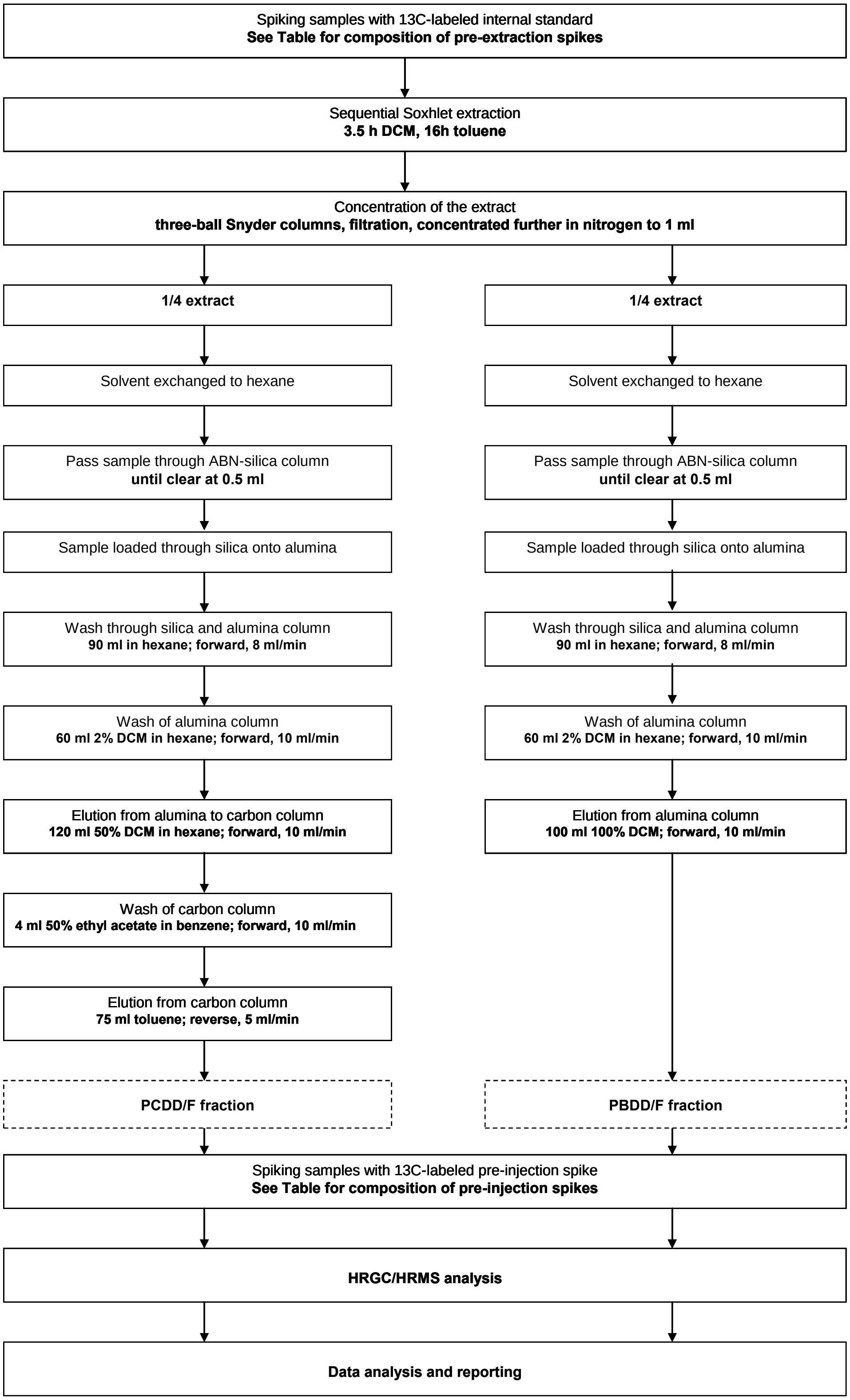

Figure 3-9. Original RTP Experimental Strategy.
The actual work added a step to the PCDD/Fs cleanup and dropped the PBDD/Fs cleanup.

3.5.3 Same-Sample Extraction of PCDD/Fs and PBDD/Fs

Extraction of sampling trains for PBDD/Fs and PCDD/Fs measurements was performed by sequential Soxhlet extraction: overnight (16 hours) with methylene chloride, followed by overnight (16 hours) extraction with toluene. This project had such a large sample volume that the regular 3.5 hours methylene chloride extraction did not give enough cycles for the extraction. Before extraction, samples were spiked with the internal standard mixtures. Pre-extraction spikes were purchased from Cambridge Isotope Laboratories Inc., Andover, Massachusetts (EDF-5408, EDF-4137A). The composition of ^{13}C-labeled PCDD/Fs and PBDD/Fs pre-extraction internal standard mixes is given in Table 3-7 and Table 3-8. All solvents were HPLC/GC/spectrophotometry grade ACS/HPLC certified (Burdick and Jackson, Honeywell, Muskegon, Michigan).

3.5.4 Cleanup and Fractionation of PCDD/Fs and PBDD/Fs

For determination of PBDD/Fs and PCDD/Fs, one-quarter of the extract was cleaned and fractionated using an automated liquid chromatography multicolumn Power Prep/Dioxin System (FMS Fluid Management Systems, Inc., Watertown, Massachusetts). One-twentieth of the extract was sent to UDRI for further analysis of other target compounds. The remainder of the extract was archived. Prior to the automated cleanup process, extracts were concentrated and then diluted in hexane, causing precipitation of non-dioxin-like compounds that could have caused interferences in the analysis. This step was repeated until no more precipitate formed and the extract was less than ten percent toluene. The extracts were then loaded and pumped sequentially through individual sets of FMS proprietary columns. Acidic and multilayer silica, carbon, and alumina columns were pre-packed, disposable cartridges available from FMS Fluid Management Systems, Inc., U.S.A. The previous experiments on HRGC/HRMS analysis of some combustion-related matrices showed interferences from other compounds that interfere with quantitative determination of the target compounds (PCDD/Fs and PCBs)[1]. This interference necessitates the introduction of an additional cleanup step, prior to the usual[2] automated PowerPrep liquid chromatography cleanup used in the OSL for same-sample determination of PBDD/Fs and PCDD/Fs from combustion flue gas. The additional step involved passing the extract through a large acidic silica gel column for the cleanup of the raw extract and concentration of the eluate to 0.5ml. This additional cleanup step was repeatedly performed until the extract was clear at 0.5ml volume. If the extract was not clear the eluate was diluted to 12ml with hexane and processed again. This clear 0.5ml of extract was then diluted to 12ml in hexane and processed through multilayer silica (4g acid, 2g base, and 1.5g neutral) column, followed by a basic alumina (11g) column and also a carbon column (0.34g). Composition of elution solutions and elution volumes are presented in Figure 3-9 of this report. To quantitate the PBDD from a single aliquot of extract, an additional step was added after the toluene elution of the carbon column, in which the alumina column was washed with 100ml of methylene chloride and that eluate was concentrated and exchanged into decane. In the later samples this portion was analyzed separately. It has been determined since the 2009 publication[2] that a separate FMS cleanup for the PBDD/Fs was not necessary, just this additional alumina

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[1] Data not published, information archived and available from OSL.

[2] Tabor D., Gullett B.K., Same-Sample Determination of Ultratrace Levels of Polybromodiphenylethers, Polybromodibenzo-p-dioxins/Furans, and Polychlorodibenzo-p-dioxins/Furans from Combustion Flue Gas. Anal. Chem. 2009, 81, 4334–4342

column wash. Also, the removal of the carbon column step completely (as was done previously) was considered insufficient cleanup for most samples. The final eluates were then spiked with pre-analysis compounds, and then decane was concentrated to a final volume of about 25µl.

3.6 Dioxin/Furan Analysis

3.6.1 HRGC/HRMS Calibration and Maintenance

EPA methods require that a laboratory record be maintained of all calibrations, including daily calibration checks. These daily checks ensure continued reliable operation and provide the operator warnings of abnormal operation.

The following calibration activities were conducted:

- Daily optimization of the HRMS instrument was carried out using a perfluorokerosene (PFK) calibration standard; static resolving power checks were performed before and after data acquisition to demonstrate the required resolution of 10 000 (5% valley).
- Bromodioxin/furan and chlorodioxin/furan calibration standard solutions (please see Section 3.5.1. for details) were used for the initial calibration of the HRGC/HRMS. The medium concentration standard was used for calibration verification according to requirements of U.S. EPA M-23.[3]
- The daily calibration was acceptable if the concentration of each labeled and unlabeled compound is within the calibration verification limit of 25-30%. If all compounds met the acceptance criteria, calibration was verified and analysis of standards and sample extracts proceeded. When any compound failed its respective limit, recalibration for all congeners was performed. In addition, the ion abundance ratios were within the allowable control limits of 15%.

Instrument maintenance was conducted as recommended by the manufacturer and on an as-needed basis. Replacement parts, including columns and filaments, were maintained in the laboratory to minimize downtime. Service engineers' visits were utilized in major failure situations and for annual preventive maintenance.

3.6.2 HRGC/HRMS Analysis

For analysis of tetra- through octa-BDD/Fs, the GC was equipped with 15m DB-5 (0.25µm film thickness × 0.25mm i.d.) column (J&W Scientific, Folsom, California). For analysis of tetra- through octa-CDD/Fs, a 60m RTX-Dioxin-2 (Restek, Bellefonte, Pennsylvania) column was used (0.25µm film thickness × 0.25 mm i.d.).

The GC oven temperature for PBDD/Fs analysis was programmed from 130°C to 320°C at 10°C/min (21 minute hold). The temperature program for PCDD/Fs went from an initial temperature of 150°C to 260°C at 10°C/min with a final hold time of 55 minutes. The carrier gas (helium) flow rates were 1 and 1.2ml/min for PBDD/Fs and PCDD/Fs, respectively. The PCDD/Fs flow was ramped to 1.5ml/min after 15 minutes. Two microliters (2µL) of the extract

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[3] U.S. EPA Test Method 23. Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors; Office of Solid Waste and Emergency Response, Environmental Protection Agency: Washington, DC, 1996.

was injected under splitless mode (injection port temperature set as 300°C and 270°C for brominated and chlorinated targets, respectively).

The HRMS was operated in an electron ionization (35 eV and 650 μA current) selective ion recording (SIR) mode at resolution $R > 10\,000$ (5% valley). The temperature of the ion source was 280°C for the PBDD/Fs analyses, whereas for PCDD/Fs, the ion source was kept at 250°C. The two strongest ions in the molecular cluster were monitored in every retention time window for each native and labeled PBDD/Fs and PCDD/Fs based on mass spectroscopy libraries and literature data, unless interferences are present. Peak responses for each of the two selected molecular ion clusters must be at least 2.5 times the noise level (S/N > 2.5), otherwise the compound was considered below the limit of detection. The bromine/chlorine isotope ratio for the two molecular ion clusters was within ±15% of the correct isotope ratio, if not they were flagged EMPC (Estimated Maximum Possible Concentration).

The standards used for PBDD/Fs identification and quantification were a commercially available set of calibration standards that contained native target tetra- through octabromodioxins and/or furans at concentrations from 0.4 to 4.0 (CS-2) through 50-500 (CS-5) ng/ml depending on the degree of bromination (EDF-5407, CIL Cambridge Isotope Laboratories Inc., U.S.A.). The standards used for chlorinated dioxin/furan identification and quantification were a mixture of standards containing tetra- to octa-PCDD/Fs native and ^{13}C-labeled congeners designed for modified U.S. EPA Method 23 (ED-2521, EDF-4137A, EDF-4136A, EF-4134, ED-4135, CIL Cambridge Isotope Laboratories Inc., U.S.A.). The PCDD/Fs calibration solutions were prepared in house and contain native PCDD/Fs congeners at concentration from 1 (ICAL-2)-20 (ICAL-6) ng/ml.

3.6.3 Data Processing and Reporting

For the data collection, Mass Lynx software (Waters, Milford, Massachusetts), version 4.1 was used (including Target Lynx 4.1. for processing and quantitation). Data processing included not only the determination of PCDD/Fs and PBDD/Fs concentrations, but also the determination of the method detection and quantitation limits (LOD and LOQ, respectively). Every set of data was reported as ng per train. For PCDD/Fs analysis, data would have been reported as ng-TEQ per train, if the analyses were accepted (pre-sampling surrogate problems will be detailed later).

3.6.4 Quality Assurance/Quality Control

The data quality objectives (DQOs) define the critical measurements needed to address the objectives of the test program, and specify tolerable levels of potential errors associated with data collection as well as the limitations of the use of the data. The data quality indicators (DQIs) are specific criteria used to quantify how well the collected data meet the DQOs. The DQI goals for the critical measurements correspond to and are consistent with the standards set forth in each respective referenced EPA Method. DQI goals will correspond to recovery criteria of the labeled standards in the respective reference methods. The DQI goals specified for the respective sampling method used by UDRI sampling team, such as pre-sampling surrogates recoveries are not included in the DQOs, but were reported to UDRI, along with quality criteria guidelines.

Composition of labeled pre-sampling (surrogate standards), pre-extraction (internal standards) and pre-injection (recovery standards) spiking solutions are given in Table 3-7 and Table 3-8.

Table 3-7. Composition of the PCDD/Fs Sample Spiking Solution

Spiking Solution	Analytes	Concentration (µg/ml)	Special Notes
Surrogate standards (Field spikes) EDF-4136A*	$^{37}Cl_4$-2,3,7,8-TCDD	1.25	Added to the sample prior to sampling
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	
	$^{13}C_{12}$-2,3,4,7,8-PeCDD	2.5	
	$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	
	$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	
Internal standards EDF-4137A*	$^{13}C_{12}$-2,3,7,8-TCDD	1.25	Added to the sample prior to extraction
	$^{13}C_{12}$-1,2,3,7,8-PeCDD	2.5	
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	2.5	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	2.5	
	$^{13}C_{12}$-OCDD	5	
	$^{13}C_{12}$-2,3,7,8-TCDF	1.25	
	$^{13}C_{12}$-1,2,3,7,8-PeCDF	2.5	
	$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	2.5	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	2.5	
Recovery Standards ED-2521*	$^{13}C_{12}$-1,2,3,4-TCDD	5	Added to extracts prior to analysis
	$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	5	

*Commercially available from CIL Cambridge Isotope Laboratories Inc., U.S.A.

Table 3-8. Composition of the PBDD/Fs Sample Spiking Solution

Spiking Solution	Analytes	Concentration (ng/ml)	Special Notes
Surrogate standard (Field spikes) EF-5410*	$^{13}C_{12}$-1,2,3,4,7,8-TeBDF	100	Added to the sample prior to sampling
Internal standards EDF-5408*	$^{13}C_{12}$-2,3,7,8-TBDD	100	Added to the sample prior to extraction
	$^{13}C_{12}$-1,2,3,7,8-PeBDD	100	
	$^{13}C_{12}$-1,2,3,4,7,8-HxBDD	250	
	$^{13}C_{12}$-1,2,3,6,7,8-HxBDD	250	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDD	500	
	$^{13}C_{12}$-OBDD	750	
	$^{13}C_{12}$-2,3,7,8-TBDF	100	
	$^{13}C_{12}$-2,3,4,7,8-PeBDF	100	
	$^{13}C_{12}$-1,2,3,4,7,8-HxBDF	250	
	$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDF	500	
	$^{13}C_{12}$-OBDF	750	
Recovery Standards EDF-5409*	$^{13}C_{12}$-1,2,3,7,8-PeBDF	100	Added to extracts prior to analysis
	$^{13}C_{12}$-1,2,3,7,8,9-HxBDD	250	

*Commercially available from CIL Cambridge Isotope Laboratories Inc., U.S.A.

3.6.5 Pre-Sampling Spikes Quality Criteria and Performance

A group of carbon-labeled PBDD/Fs and PCDD/Fs congeners (Table 3-7. and Table 3-8) were added to the PUF sorbent before the sample was collected in UDRI. The surrogate recoveries were measured as relative to the internal standards and were a measure of the sampling train collection efficiency.

OSL provided results of pre-sampling spikes recovery to UDRI, using the acceptance criteria outlined in Table 3-9.

Table 3-9. Pre-Sampling Spike Recovery Limits [%]

Pre-sampling spike	Minimum	Maximum
PCDD/Fs	%	%
$^{37}Cl_4$-2,3,7,8-TeCDD	70.0	130
$^{13}C_{12}$-2,3,4,7,8-PCDF	70.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	70.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	70.0	130
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	70.0	130
PBDD/Fs	%	%
$^{13}C_{12}$-1,2,3,4,7,8-TeBDF	70.0	130

The pre-sampling surrogates recovery acceptance criteria were as recommended by U.S. EPA Method 23 for chlorinated dioxins.[4] There is no standard method guidance for PBDD/Fs pre-sampling surrogates recovery; hence Method 23 acceptance criteria were used for brominated targets.

Upon analysis of the PCDD/Fs samples, the pre-sampling surrogates were found to be absent from seven of the ten samples requested for PCDD/Fs analysis. Because this constituted a large majority of the PCDD/Fs samples and that there were no PCDD/Fs detected in the first phase of this project, the investigators decided not to report PCDD/Fs data. In the samples that were analyzed, there were virtually no PCDD/Fs detected consistent with the first phase of the project but it would be consistent with complete loss of target compounds which is highly unlikely given the PBDD/Fs data. Given both of these possibilities, not reporting the data was of the most objective action.

There was significant brominated interference in 6 of 18 tests. The six tests with bromine interference were all the samples that had standard halogen-containing ground components added. This reduced the number of measured experimental samples to 12. In the PBDD/Fs samples there was also a brominated pre-sampling surrogate. The recoveries for the 12 samples ranged from 0.8% recovery to 234% recovery. Four samples appear to have been double-spiked with recoveries near 200% and the sample near 0% recovery was probably not spiked. Five of the remaining samples were between 90 and 110% recovery. The other two samples had low recovery which was not likely due to spiking problems.

3.6.6 Pre-Extraction Spikes Quality Criteria

A group of 11 PBDD/Fs and 9 PCDD/Fs ^{13}C-labeled internal standards (see Table 3-7. and Table 3-8), representing the tetra- through octa-halogenated homologs, were added to every sample

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[4] U.S. EPA Test Method 23. Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors; Office of Solid Waste and Emergency Response, Environmental Protection Agency: Washington, DC, 1996.

prior to extraction. The role of the internal standards is to allow quantification (via the isotope dilution internal standard methodology) of the native targets in the sample as well as to determine the overall method efficiency.

Recovery criteria for the internal standards of PBDD/Fs and PCDD/Fs are given in Table 3-10.

Table 3-10. Pre-Extraction Spike Recovery Limits [%]

Pre-extraction spike	**Minimum**	**Maximum**
PCDD/Fs	%	%
$^{13}C_{12}$-2,3,7,8 TeCDF	40.0	130
$^{13}C_{12}$-2,3,7,8 TeCDD	40.0	130
$^{13}C_{12}$-1,2,3,7,8 PCDF	40.0	130
$^{13}C_{12}$-1,2,3,7,8 PCDD	40.0	130
$^{13}C_{12}$-1,2,3,6,7,8 HxCDF	40.0	130
$^{13}C_{12}$-1,2,3,6,7,8 HxCDD	40.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8 HpCDF	25.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8 HpCDD	25.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8,9 OCDD	25.0	130
PBDD/Fs	%	%
$^{13}C_{12}$-2,3,7,8-TBDF	40.0	130
$^{13}C_{12}$-2,3,7,8-TBDD	40.0	130
$^{13}C_{12}$-2,3,4,7,8-PeBDF	40.0	130
$^{13}C_{12}$-1,2,3,7,8-PeBDD	40.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxBDF	40.0	130
$^{13}C_{12}$-1,2,3,4,7,8-HxBDD	40.0	130
$^{13}C_{12}$-1,2,3,6,7,8-HxBDD	40.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDF	25.0	130
$^{13}C_{12}$-1,2,3,4,6,7,8-HpBDD	25.0	130
$^{13}C_{12}$-OBDD	25.0	130
$^{13}C_{12}$-OBDF	25.0	130

The pre-extraction internal standard recovery acceptance criteria were as recommended by U.S. EPA Method 23 for chlorinated dioxins.[5] There is no standard method guidance for PBDD/Fs pre-extraction internal standards recovery; U.S. EPA Method 23 criteria were therefore used for brominated targets.

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[5] U.S. EPA Test Method 23. Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors; Office of Solid Waste and Emergency Response, Environmental Protection Agency: Washington, DC, 1996.

As was mentioned before, the PCDD/Fs results were considered not reportable and the pre-extraction results are not reported as well.

The brominated pre-extraction spikes mostly passed the PCDD/Fs criteria up to the hexa congeners but the hepta and octa congeners were frequently below the PCDD/Fs criteria although detectable. In the original QAPP, the table for the PBDD/Fs pre-extraction spike criteria was not the table of criteria specified in the Method 23 for PCDD/Fs pre-extraction spikes (Table 3-10).

3.7 Polyaromatic Hydrocarbon Analysis

Combustion by-products were collected into PUF and filter and Soxhlet extracted using both methylene chloride and toluene, yielding two separate samples for analysis. The sampling train was also rinsed sequentially with methanol, methylene chloride, and toluene following each experiment to collect any by-products that may not have been collected by the PUF or filter. The methanol rinse was solvent extracted with the methylene chloride rinse (liquid-liquid extraction) and separated, yielding two separate samples from the three rinses. Therefore, UDRI tested four different sample media for the presence of PAHs: (1) methylene chloride from methanol and methylene chloride rinses, (2) toluene rinse, (3) methylene chloride Soxhlet extraction of PUF and filter, and (4) toluene Soxhlet extraction of PUF and filter. Using samples from brominated laminate tests, the PAH content of the rinses were compared to the PAH content of the PUF/filter extracts. Methylene chloride and toluene rinses from experiments with BFR + P - 50 (E6), BFR - 100 (E15), and BFR + PHF - 50 (E30) were analyzed (for Experiment # see Appendix B: Experimental Conditions). Experiment BFR - 100 (E15) was used to analyze the toluene rinse and was compared to the extract. For methylene chloride, most of the PAHs (EPA list of priority PAHs) in the rinse were estimated to be <10% of the magnitude of the PAHs from the extract. This excludes naphthalene and compounds lighter than fluorine where breakthrough was likely. The naphthalene and lighter compounds were less than 1% in the rinses when compared to the PUF/filter extracts. Even in the extract, the naphthalene signal was significantly smaller than the other PAHs detected probably due to breakthrough through the PUF. UDRI found ~90% of the PAHs to be in the methylene chloride extracts compared to <10% in the methylene chloride rinses. The level of PAHs detected in the toluene extract was <1% and in the toluene rinse was <0.1%. These findings and budgetary constraints led the researchers to decide to only analyze the methylene chloride extracts. PAHs were thus only measured for the methylene chloride extraction samples for the remainder of the project.

3.8 Organophosphorus and Chlorinated Benzene/Phenol Analysis

The chromatograms from PAH analysis were used to generate library search reports to determine the presence of organophosphorous compounds. In addition, since no attempt was made to analyze for chlorinated dioxins and furans due to reasons explained in Section 3.6.5, an attempt was made to determine the presence of chlorinated benzenes and phenols known to be precursors for the formation of halogenated dioxins and furans. The following integration events were used when generating the library search reports: initial area reject at 1%; initial peak width of 0.02; shoulder detection off; initial threshold of 16. The compound with the highest match quality is reported for the compounds detected.

4 Results and Discussion

The purpose of this study as part of the U.S Environmental Protection Agency (EPA) Design for the Environment (DfE) program was to understand the potential emissions of halogenated dioxins or furans, and polyaromatic hydrocarbons (PAHs) from burning circuit board laminates. This objective was achieved by using the cone calorimeter to expose circuit board laminates to simulated combustion scenarios under ventilated fire conditions (15 L/s) at two heat fluxes (50 kW/m^2 and 100 kW/m^2). The 50 kW/m^2 heat flux was chosen to mimic open burn conditions when circuit boards are improperly burned for precious metal recovery. The higher heat flux, 100 kW/m^2, was chosen to mimic incineration conditions that would be used to recover/smelt away precious metals and properly dispose of e-waste. Since the sampling train for this study prevented the normal collection of oxygen consumption calorimetry data (Sections 3.3.1 to 3.3.3), experiments were done using the normal cone calorimeter exhaust system to collect data for heat release (see Appendix A: Circuit Board Flammability Data), smoke yield, fire safety information, oxygen consumption rates, CO/CO_2 production rates, and effective heats of combustion needed to attempt to correlate back to observed emission products. The emphasis of this section of the report is on the emissions observed from the cone calorimeter (smoke, CO/CO_2) which will then be later compared to the emissions data collected from the sampling train.

4.1 Total Mass Burned

The total mass of each type of printed circuit board laminate sample burned for the cone calorimeter total sampling train experiments is given in Table 4-1. Total mass is important for determining emissions factors; the amount of flammable mass burned will determine how much total emissions are obtained.

Table 4-1. Total Mass Burned Per Sample

Sample Description-Heat Flux (kW/m^2)	Total Mass Burned per Sample (g)
BFR - 50	11.8
BFR - 50	13.6
BFR - 100	14.3
BFR - 100	15
BFR + P - 50	20
BFR + P - 50	20.4
BFR + PHF - 50	18.2
BFR + PHF - 50	17.3
HFR - 50	8.9
HFR - 50	8.1
HFR - 100	13.3
HFR - 100	13.3
HFR + P - 50	18.1
HFR + P - 50	19.8
HFR + PHF - 50	19.6
HFR + PHF - 50	18.6
1556 HFR - 50	9.3
1556 HFR - 50	9.7
1556 HFR + P - 50	17.9
1556 HFR + P - 50	17.8
1556 HFR + PHF - 50	16.4
1556 HFR + PHF - 50	15.9
NFR - 50	16.5
NFR - 50	15.6
NFR - 100	7.9
NFR - 100	8.8

4.2 Smoke

Smoke data obtained using the standard cone calorimeter (without the total sampling train) for all of the printed circuit board samples are shown in Table 4-2. Total smoke release was affected by both component blend and flame retardant chemistry, with flame retardant chemistries always having higher smoke release than the non-flame retardant samples. It should be noted that smoke release in the cone calorimeter is a simple light obscuration measurement and may be composed of many different components. While smoke is a good indication of incomplete combustion, its presence cannot be directly correlated to emissions of concern (PM, PAH, dioxins, etc.). Instead, smoke provides some insight into likely emissions trends from the different flame retardant chemistries.

Table 4-2. Smoke Release Data

Sample Description-Heat Flux (kW/m^2)	Average smoke release. N=3 per sample* (m^2/m^2)
NFR - 50	222.03
BFR - 50	479.10
HFR - 50	250.80
1556 HFR - 50	246.33
NFR - 100	214.73
BFR - 100	439.77
HFR - 100	264.83
BFR + P - 50	691.80
HFR + P - 50	438.53
1556 HFR + P - 50	397.43
BFR + PHF - 50	468.13
HFR + PHF - 50	353.43
1556 HFR + PHF - 50	309.23

* Raw data listed in appendix

The smoke release information is also presented in Figure 4-1 and the following conclusions can be made.

Brominated Flame retardant (BFR) – When compared to the other chemistries, BFR smoke release was more than 50 to 90% greater than HFR samples. This is expected due to the flame retardant mechanism of BFR which inhibits vapor phase combustion and in turn creates more smoke. As heat in the flame increases due to higher heat flux, more of the smoke should burn away and total smoke should decrease; this is observed in Figure 4-1.

Halogen-Free Flame retardant (HFR) **and** ***1556 Halogen-Free Flame retardant (1556 HFR)*** – Due to the mechanism of flame retardancy, which should be condensed phase char formation assuming that the halogen-free flame retardants are phosphorus-based, lower smoke release is observed compared to the BFR laminates. Unlike the BFR laminates, as heat flux is increased for HFR, a slight increase (5.6 %) in total smoke was observed compared to NFR(-4.6%). This may be due to the fact that the higher heat flux of burning is causing more of the PAHs in the char of the samples to become pyrolyzed and form soot and condensed phase soot precursors. However, this difference between NFR and HFR samples is within the percentage error of the cone calorimeter smoke measurement device (± 10%). The difference should be considered with caution even though the trend was reproducible with the triplicate cone calorimeter experiments conducted.

No Flame retardant (NFR) – These materials show the lowest smoke release as expected since they have no flame retardants present. However, the difference compared to HFR is within the margin of error of the measurement device as described above.

Halogenated and Low-Halogen Components – The addition of powdered components produced variable smoke release results (-2.2 to 74.6 %) compared to the laminates alone. For example, the addition of halogen containing components to BFR increased smoke by 44.2%, but when low-halogen component powders were present, total smoke was reduced by 2.2%. The addition of halogen containing components to halogen-free laminates provided the highest increases in smoke release 74.6% and 61.3% for HFR and 1556 HFR laminates respectively. Halogen-free component powders yielded a smaller increase in smoke compared to the halogen-containing component powders, with a reduction in total smoke (2.2%) seen with BFR laminates, and only a 40.9% and 25.6% increase for HFR and 1556 HFR laminates respectively. The extra flammable mass in both powders contributes to some smoke from burning, but the presence of halogen increased smoke release even more.

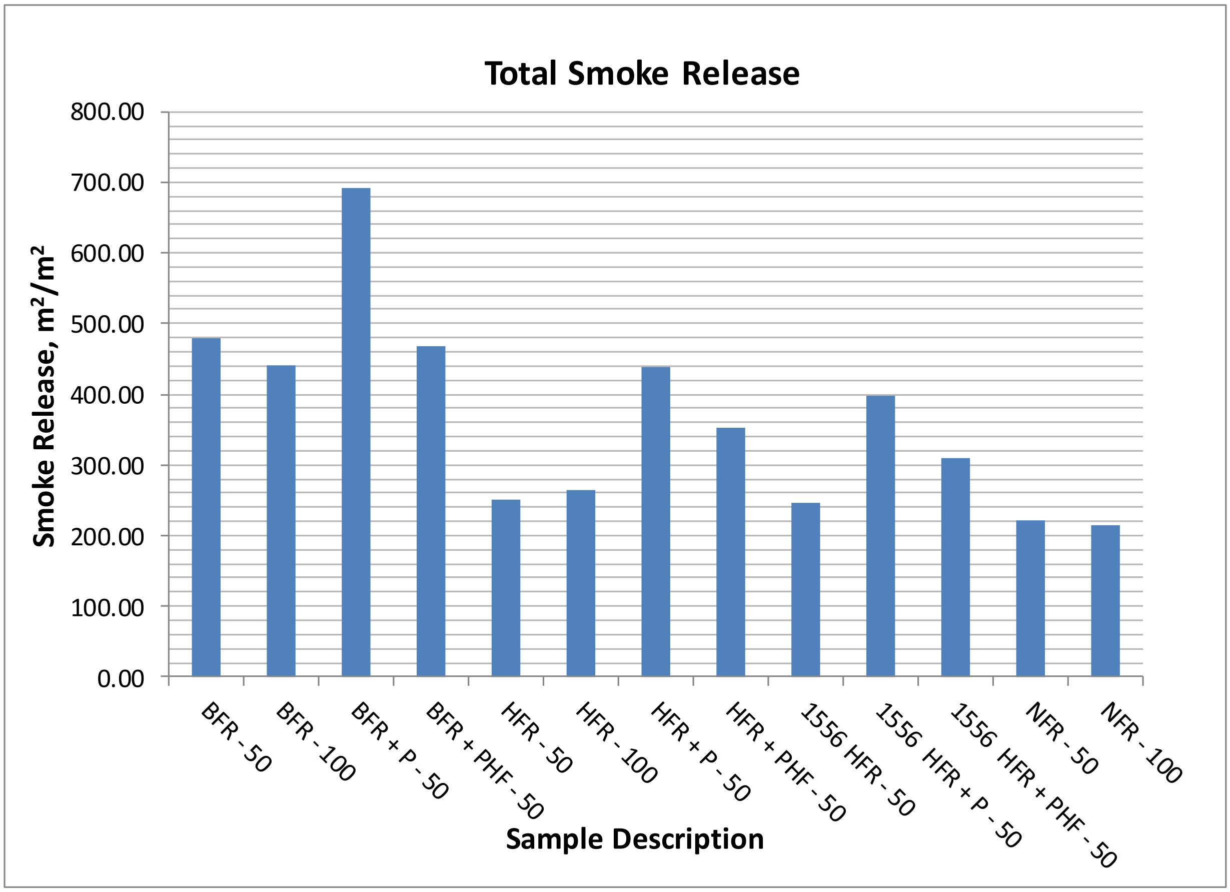

Figure 4-1. Smoke Release Plot

4.3 CO/CO_2 Emissions

The brominated FR laminates, with or without components, show lower emissions of CO_2 than the other sample types (1.05 to 1.28 kg/kg compared to 1.3 to 1.62 kg/kg for HFR and 1.85 and 1.67 kg/kg for NFR) (Table 4-3 and Figure 4-2). Less total CO_2 is observed because bromine inhibits full combustion of carbon to CO_2. However, a significant increase in CO is not always observed with the samples tested in this study when CO_2 emissions decrease. Therefore, the data only support the idea that the brominated FR compounds reduce total CO_2 emissions when combusted under open burn (50 kW/m^2 heat flux) or incinerator (100 kW/m^2 heat flux) conditions. The mass balance of emissions must lie in other gases and compounds if the CO_2 emissions are lower. The non-halogenated FR laminates have similar CO yields when compared to the BFR compounds, but higher CO_2 yields. This makes sense in that the flame retardants are causing more char formation, which would lower the total amount of carbon that is combusted. Since the non-halogenated laminates do not contain halogens that can affect combustion chemistry, CO_2 yields should be higher. The non-flame retardant samples burn with the highest CO_2 yields but have CO emissions roughly equal to or higher than the other flame retardant systems when burned at low heat flux (50 kW/m^2). This is because in the flame retardant systems, potential carbon is present as PAHs and soot rather than being partly oxidized. Total mass burned (total potential carbon that could convert to CO or CO_2; see **Table 4-1**) does not seem to correlate well to average CO and CO_2 emissions, allowing combustion chemistry of the boards, flame retardants, and components to explain to CO/CO_2 emissions factors.

Table 4-3. CO/CO_2 Emission Factors

	Av Post Ignition	
	CO Yield	CO_2 Yield
Sample Description-Heat Flux (kW/m^2)	(kg/kg)	
BFR - 50	0.15	1.05
BFR - 100	0.14	1.06
BFR + P -50	0.13	1.12
BFR + PHF - 50	0.14	1.28
HFR - 50	0.18	1.59
HFR - 100	0.11	1.44
HFR + P - 50	0.16	1.50
HFR + PHF - 50	0.12	1.52
1556 HFR - 50	0.12	1.42
1556 HFR + P - 50	0.10	1.30
1556 HFR + PHF - 50	0.10	1.62
NFR - 50	0.20	1.85
NFR - 100	0.07	1.67

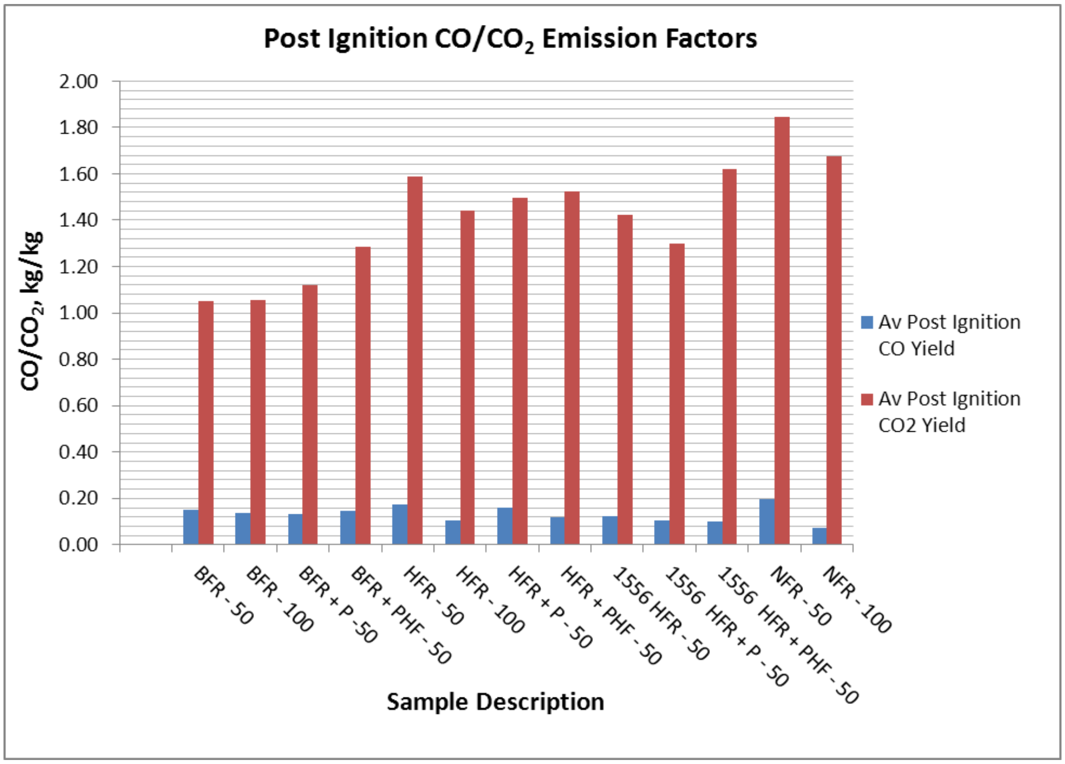

Figure 4-2. CO/CO$_2$ Emission Factors Plot

4.4 Particulate Matter Emissions

The cone calorimeter data (Table 4-4 and Figure 4-3) demonstrates that most of the samples have similar PM emissions when components are present, but can vary depending on base resins. The halogen-free flame retardant (HFR) at 50 kW/m^2 has the highest level (40% higher than BFR 50 kW) of PM emitted during burning. This relates to the condensed phase mechanism of action, where the phosphorous flame retardant reacts with the polymer and is involved in its charring. These charred and cross-linked polymer components will have chemical structures similar to soot precursors, and as those molecules pyrolyze off the surface of the burning circuit board, higher amounts of PM may be seen. The BFR compounds do show some higher PM emissions when compared to the NFR and HFR + component blends. While smoke yields were higher for BFR compounds compared to other sample types (Table 4-2 and Figure 4-1), PM was not always higher for BFR. This may simply indicate that the smoke produced by burning BFR materials is not captured by the PM filters in our experiments or that the smoke measured by the cone calorimeter system was not a particulate but was instead organic vapors which obscured light.

Table 4-4. PM Emission Factors

Sample Description-Heat Flux (kW/m^2)	**PM, g/kg fuel in**
BFR - 50	24.05
BFR - 100	23.11
BFR + P - 50	22.66
BFR + PHF - 50	20.85
HFR - 50	33.48

Sample Description-Heat Flux (kW/m^2)	PM, g/kg fuel in
HFR - 100	21.02
HFR + P - 50	18.59
HFR + PHF - 50	19.32
1556 HFR - 50	23.54
1556 HFR + P - 50	17.93
1556 HFR + PHF - 50	13.42
NFR - 50	17.28
NFR - 100	17.70

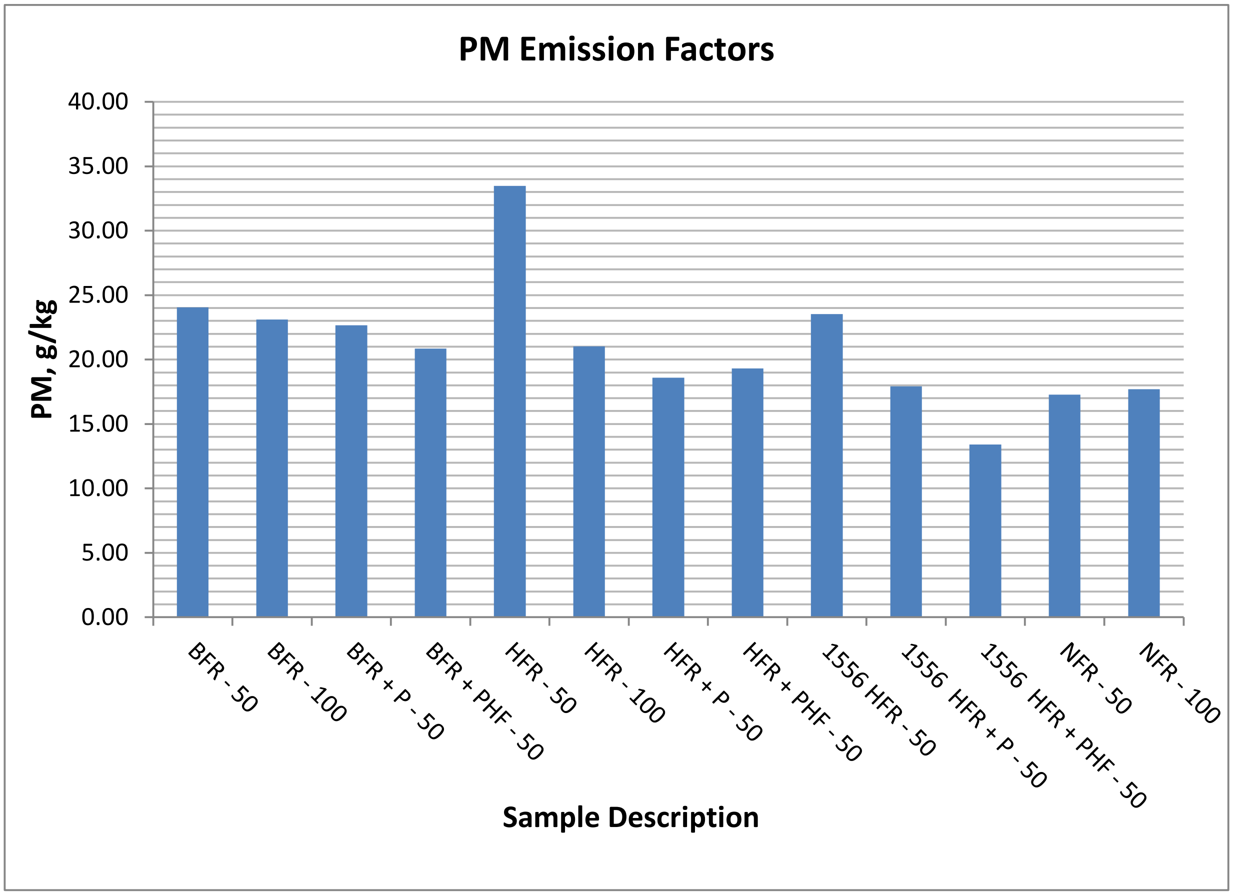

Figure 4-3. Particular Matter (PM) Emission Factors

4.5 PBDD/Fs and PCDD/Fs Emission Factors

Printed circuit board combustion at UDRI generated 42 samples for analysis. Not all samples were analyzed for PCDD/Fs and PBDD/Fs due to resource limitations; instead a relevant subset of samples was selected for analysis. The laminate samples containing brominated flame retardant tested at 50 kW/ m^2 alone and with halogenated components or with low halogen components, and at 100 kW/m^2 alone, and the necessary blanks were analyzed for PCDD/Fs and PBDD/Fs. This approach resulted in nine samples being selected for PCDD/Fs analysis, and 14 samples selected for PBDD/Fs analysis at EPA. Due to problems with the pre-sampling spike, the PCDD/Fs analysis was not quantitated. In the PBDD/Fs analysis, four blanks were added to the fourteen samples selected, yielding 18 samples. Of the 18 total samples, 12 were able to be quantitated. The six samples that could not be quantitated were of brominated flame retardant with halogenated components. The quantitation could not be done due to significant interference that caused the internal standards to not be useable for quantitation. Analysis of one sample on a LRMS in full scan resulted in insufficient sensitivity to identify the compound emissions.

PBDD/Fs compounds were quantitated in 12 samples. Six of these samples were BFR laminates and six were combustion blanks. Five of the six blanks had significantly lower levels of PBDD/Fs compared to the laminate samples. For the higher concentrated PBDD/Fs detected, the difference in detection level between the combustion blanks and the BFR laminates was as large as a factor of 100. For example, the detection of 1,2,3,4,6,7,8 - HpBDF in all but the first blank ranged from not detected to 0.3 ng/train compared to 4 to 9 ng/train for the six BFR laminate samples. In a system that is as complex as the calorimeter and has as many reused parts very low levels in the actual heated calorimeter blanks are not surprising.

The chromatographic peaks for the 2,3,7,8 congeners were small compared to the non-2,3,7,8 congeners based on visual confirmation. This finding was confirmed by quantification of a single non-2,3,7,8 congener. 2,4,6,8-TeBDF congener was a factor of four higher than the highest of the 2,3,7,8-Br-substituted toxic congeners in the samples. Other visible brominated compounds in the chromatograms were of similar concentrations.

The total PBDD/Fs emission from the cone calorimeter experiments shown in Table 4-5 and Figure 4-4 indicate that brominated flame retardant (BFR) laminates have higher total PBDD/Fs emission factors than brominated flame retardant laminates with halogen-free components. For all six brominated samples, PBDD/Fs were released in the range of 1.89 to 4.14 ng/g (Table 4-5) with variability that suggests there is no large difference between each sample based on only N=2. Figure 4-4 is based on the average emission factors and suggest differences in the samples that cannot be conclusive without larger sample sizes.

Brominated dioxins and furans were not analyzed in the NFR and HFR systems since these systems were free of brominated FR structures (TBBPA) that could have formed PBDD/Fs compounds.

Interestingly, the addition of components did not appear to increase PBDD/Fs emissions. This may due to (1) a chemical interaction between the halogen-free component powder and PBDD/Fs, (2) a dilution effect from the additional non-halogenated mass burned contributing to the total mass lost used in the emission factor calculation, or (3) a combination of both. At this time, it is not be possible to clearly discern given the data scatter between the replicates shown in Table 4-5.

Based on the available data, the conclusion is that PBDD/Fs are detected in the emissions of these brominated samples.

Table 4-5. PBDD/Fs Emission Factors

Analyte	Sample Description - Heat flux (kW/m^2)					
	BFR - 50	**BFR - 50**	**BFR - 100**	**BFR - 100**	**BFR + PHF-50**	**BFR + PHF-50**
ND=0,EMPC=EMPC	**ng/g**					
2,3,7,8 - TBDD	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1,2,3,7,8 - PeBDD	3.72E-01	1.79E-01	1.85E-01	3.25E-01	1.20E-01	1.42E-01
1,2,3,4,7,8 + 1,2,3,6,7,8 - HxBDD	1.38E-01	9.57E-02	1.25E-01	1.49E-01	8.79E-02	6.94E-02
1,2,3,7,8,9 - HxBDD	6.97E-02	4.68E-02	5.45E-02	7.65E-02	4.49E-02	3.16E-02
1,2,3,4,6,7,8 - HpBDD	8.76E-02	7.73E-02	1.42E-01	1.18E-01	7.36E-02	7.18E-02
1,2,3,4,6,7,8,9 - OBDD	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
2,3,7,8 - TBDF	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1,2,3,7,8 - PeBDF	5.81E-01	0.00E+00	1.59E-01	2.24E-01	2.42E-01	2.79E-01
2,3,4,7,8 - PeBDF	8.90E-01	5.14E-01	2.47E-01	4.06E-01	3.60E-01	6.11E-01
1,2,3,4,7,8 - HxBDF	1.32E+00	6.60E-01	2.29E-01	9.04E-01	4.86E-01	5.72E-01
1,2,3,4,6,7,8 - HpBDF	5.68E-01	3.45E-01	4.21E-01	6.25E-01	2.48E-01	3.11E-01
1,2,3,4,6,7,8,9 - OBDF	7.35E-02	5.57E-02	-	0.00E+00	0.00E+00	0.00E+00
Total PBDD/Fs (ND=0; EMPC= 0)	3.21E+00	1.97E+00	1.56E+00	2.83E+00	1.66E+00	2.06E+00
Total PBDD/Fs (ND=0; EMPC= EMPC)	4.10E+00	1.97E+00	1.56E+00	2.83E+00	1.66E+00	2.09E+00
Total PBDD/Fs (ND=DL; EMPC= EMPC)	4.14E+00	2.05E+00	1.89E+00	3.07E+00	2.09E+00	2.63E+00

The laminate samples with halogenated components (BFR-P) could not be quantitated due to significant halogenated interference.

"EMPC" indicates that the bromine isotope ratio for the two molecular ion clusters was not within ±15% of the correct isotope ratio. When the two molecular ions are not within the correct isotope ratio, the two molecular ions are quantitated separately and the smaller quantitation is denoted EMPC. The EMPC notation identifies that the presence of an additional molecule may be influencing the detection level of the compounds of interest.

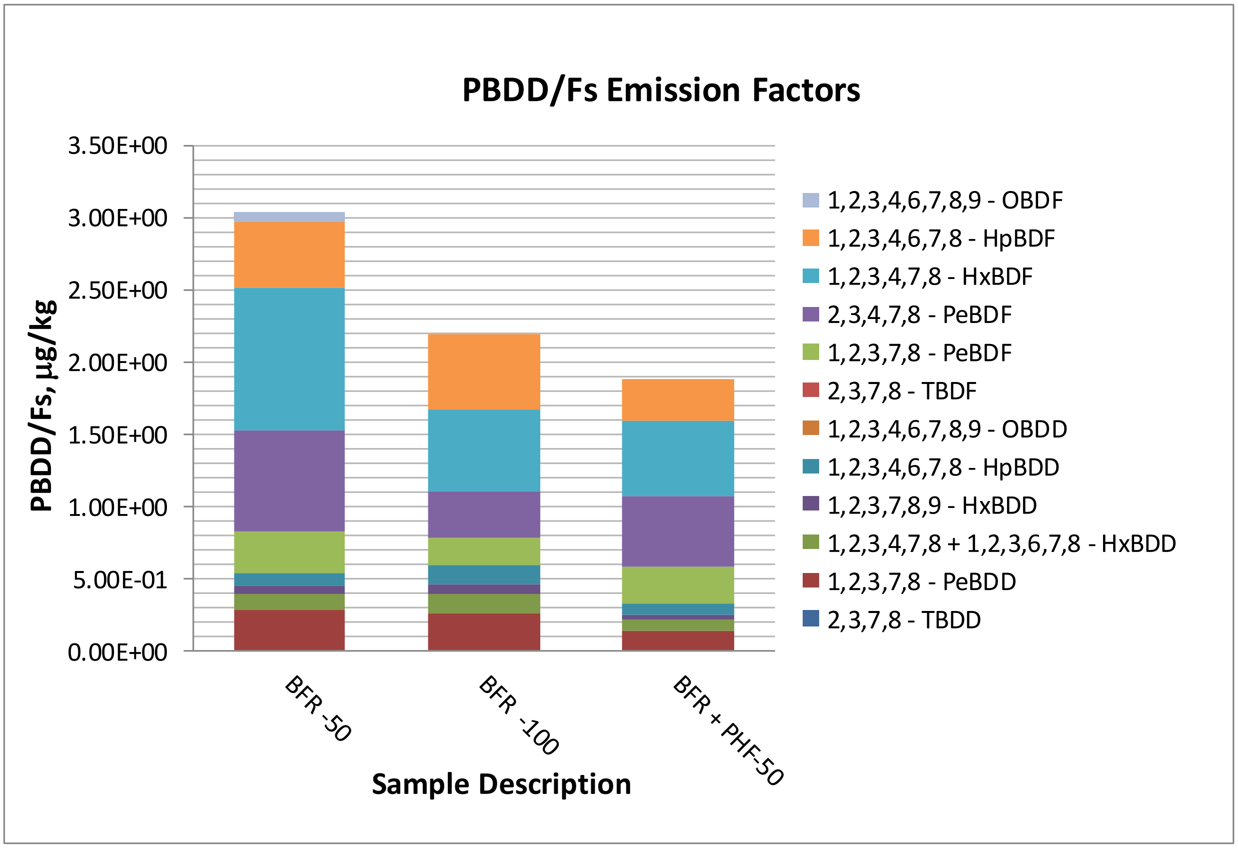

Figure 4-4. PBDD/Fs Emission Factors Plot for ND=0 and EMPC=EMPC
The laminate samples with halogenated components (BFR + P) could not be quantitated due to significant interference.

4.6 PAH Emissions

Table 4-6, Table 4-7 and Figure 4-5 show the total PAH emission factors for the 16 EPA priority PAHs quantified for the different printed circuit board laminates tested using the cone calorimeter. Brominated flame retardant (BFR) laminates burned at 50 kW/m^2 heat flux had the highest total PAH emissions and no flame retardant (NFR) laminates burned at 50 kW/m^2 heat flux had the least. At a higher heat flux (100 kW/m^2), the NFR sample showed 29% higher PAH emissions than the halogen-free (HFR) sample at the same heat flux. Emissions for the BFR were similar at both heat flux levels.

The observed trends of PAH emissions make sense in light of both the known and assumed flame retardant mechanisms for the two types of flame retardant systems. Since the BFR is a vapor phase flame retardant, any combustion of that flame retardant with decomposing epoxy structures should generate more incomplete combustion products. In the case of the HFR system, it is assumed a phosphorus-based flame retardant is present, which has more of a condensed phase (char formation) mechanism and binds up most of the possible PAH structures on the burned sample residue rather than created in the flame front as seen with BFRs. The results presented in Figure 4-5 support this general trend with a wide range of PAH products detected. The presence of component powders affected PAH emissions for both BFR and HFR systems. PAH emissions were reduced for the 1556 HFR samples that had components compared to the other HFR samples. In some cases, a slight increase in PAH emissions was noted for the other HFR laminates when components were present. For the BFR systems, the presence of components slightly lowered total PAH emissions.

Since PAHs are known to be the nascent precursors of soot, a higher presence of PAHs should lead to higher PM yields from combustion. In this study, the PM yields (Table 4-4 and Figure 4-3) and the PAH emissions (Table 4-6 and Figure 4-5) did not always have this positive correlation. Typically, naphthalene yields should have been higher than the other PAHs detected. Analysis of our methods to determine breakthrough of PAHs during sampling at these high velocities has shown that fluorene and heavier compounds are captured using 4 PUFs in the glass cartridge that holds the PUFs and that acenaphthylene breakthrough was almost 50%. However, since the carcinogenic PAHs are of interest and the extraction of eight PUFs is complex, no attempt was made to prevent breakthrough of compounds lighter than fluorene by increasing the number of PUFs. Figure 4-6 displays the PAH emissions data excluding compounds with a lower molecular weight than fluorene likely to have had breakthrough. The same emission trends were observed when naphthalene, acenapthylene, and acenapthene were excluded, suggesting that no crucial information was lost by not sampling compounds requiring eight sampling PUFs.

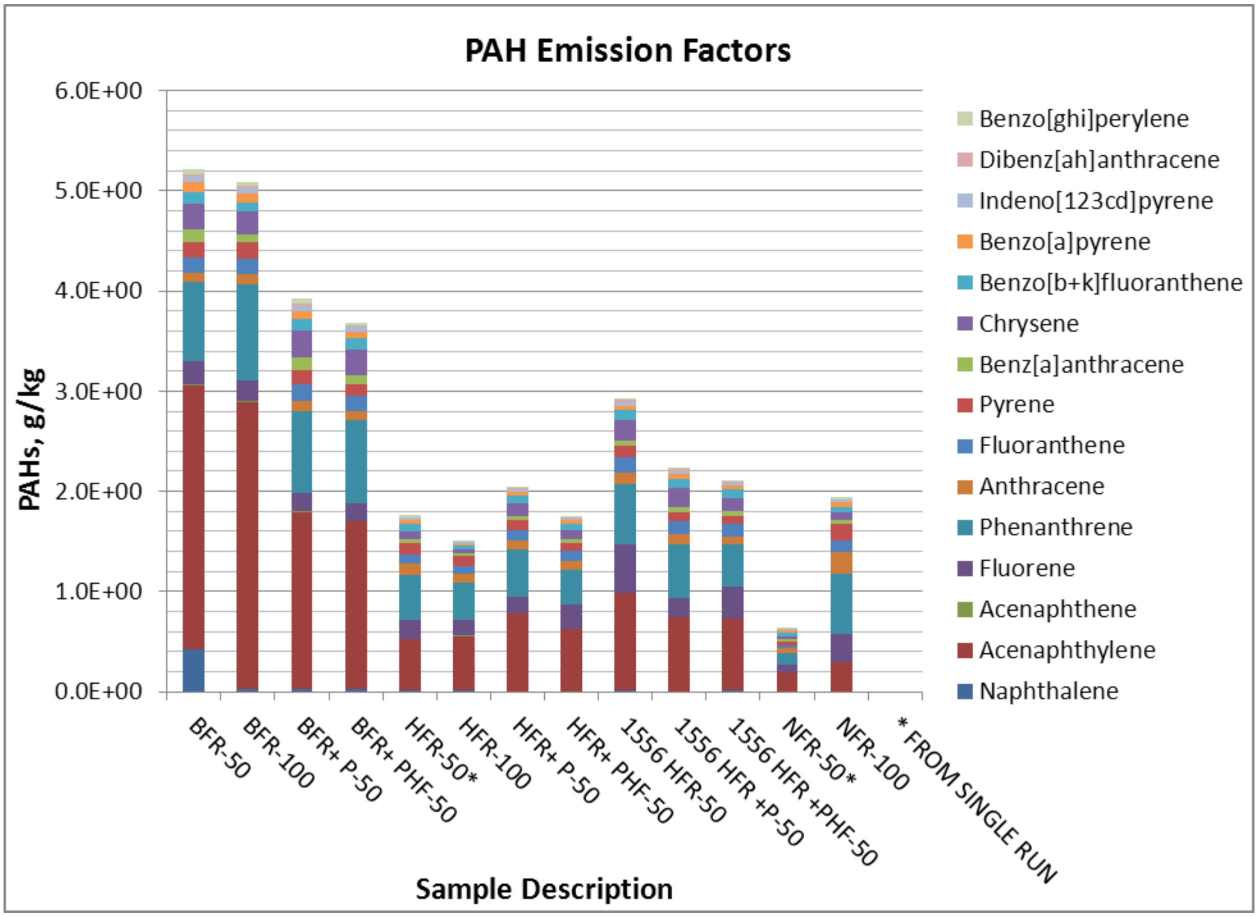

Figure 4-5. PAH Emission Factors Plotted for Naphthalene and Higher Molecular Weight PAHs Detected from the EPA List of 16‡ Priority PAHs

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

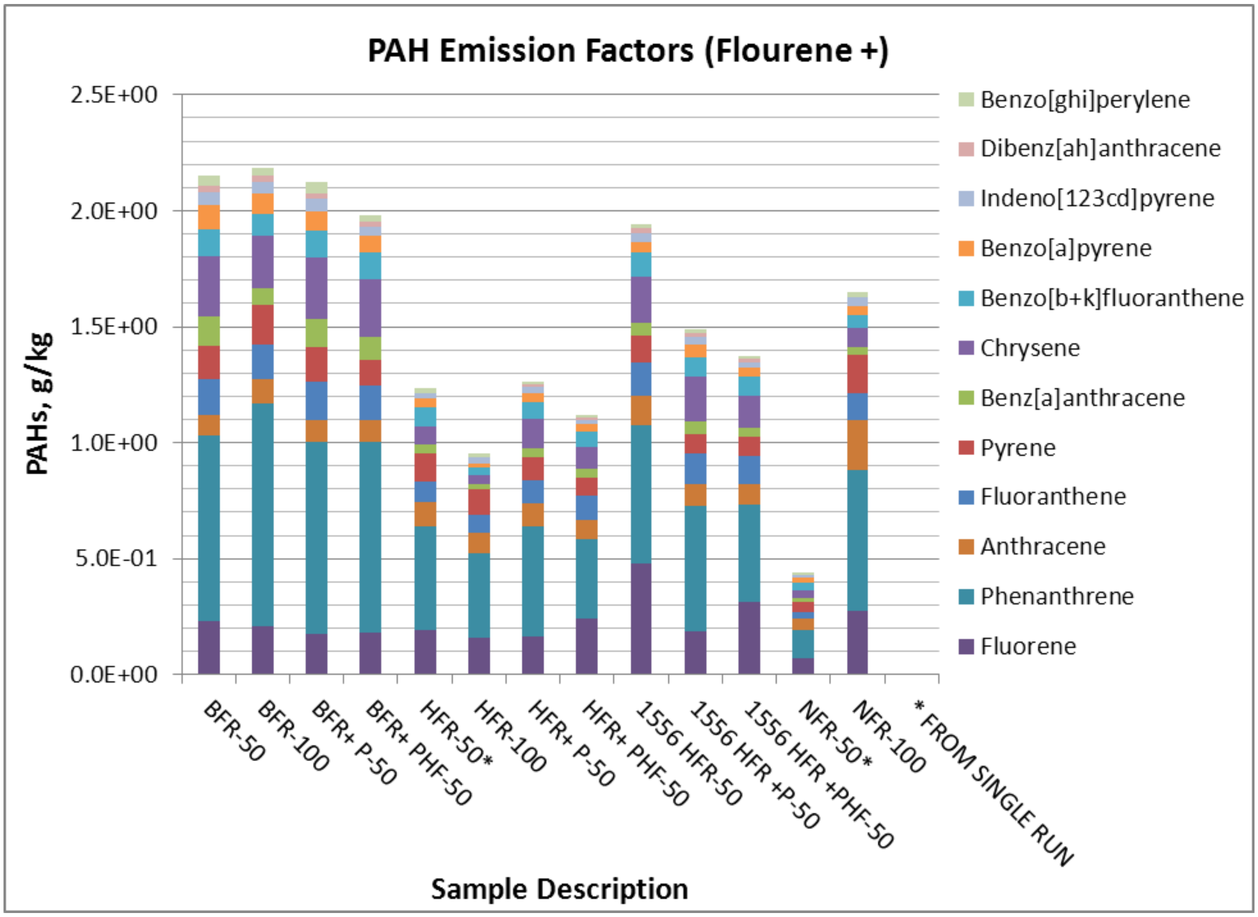

Figure 4-6. PAH Emission Factors for Fluorene and Higher Molecular Weight PAHs Detected from the EPA List of 16‡ Priority PAHs

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

When looking solely at the release of known carcinogenic PAHs (Figure 4-7), trends similar to those in Figure 4-5 and Figure 4-6 are observed. BFR systems produce more of the carcinogenic PAHs than the HFR or NFR systems. The addition of components does not appear to drastically affect the yields of carcinogenic PAHs. The presence of components decreases the yields in some cases probably due to a dilution effect from the added mass when calculating emission factors. The high heat flux can cause the NFR system to give off just as much carcinogenic PAHs as a flame retardant + component system from a lower heat flux. When looking at only the toxic equivalent emission factors of carcinogenic PAH values (Figure 4-8), it is again observed that BFR has the highest value followed by the HFR systems and then the NFR system.

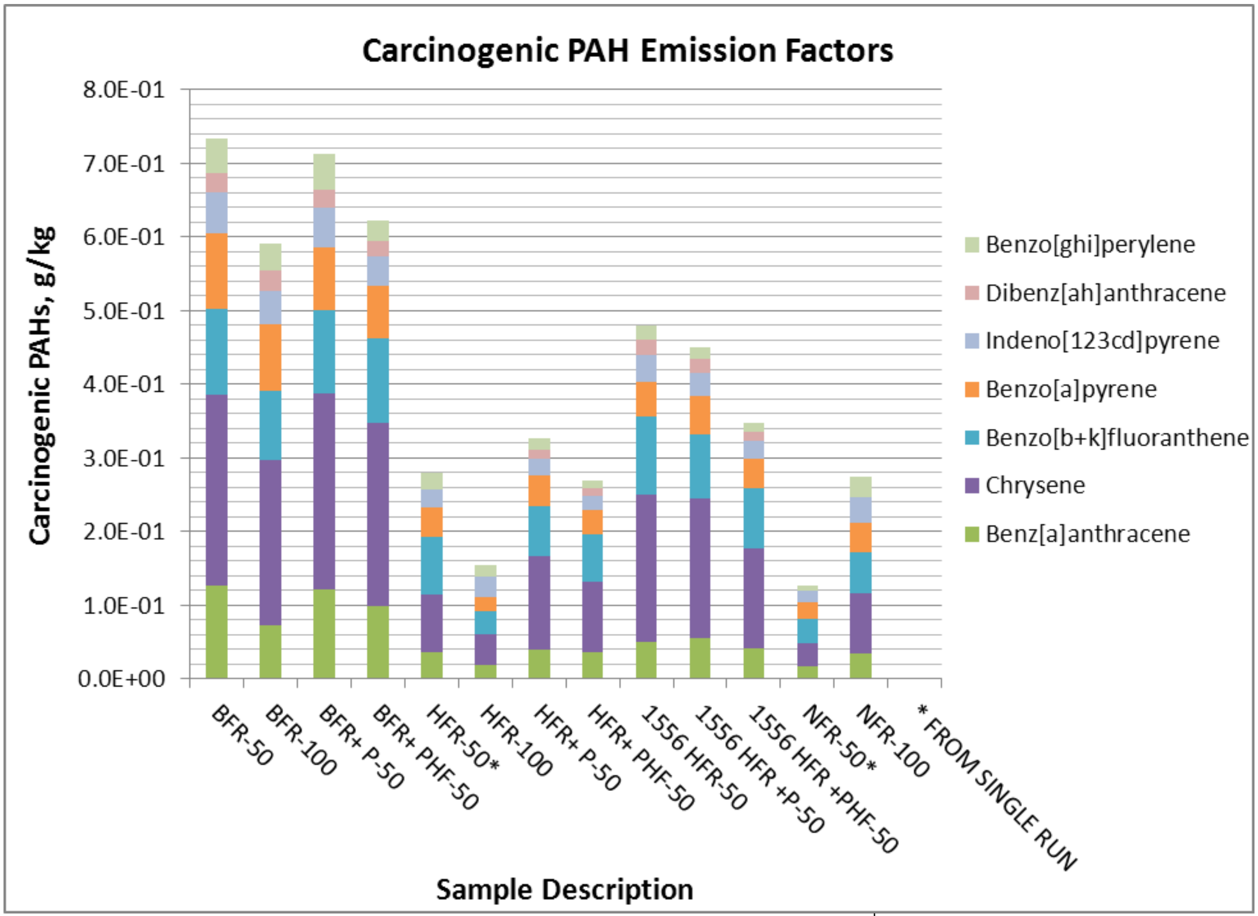

Figure 4-7. Emission Factors of Carcinogenic PAHs from the EPA List of 16[‡] Priority PAHs

[‡] Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

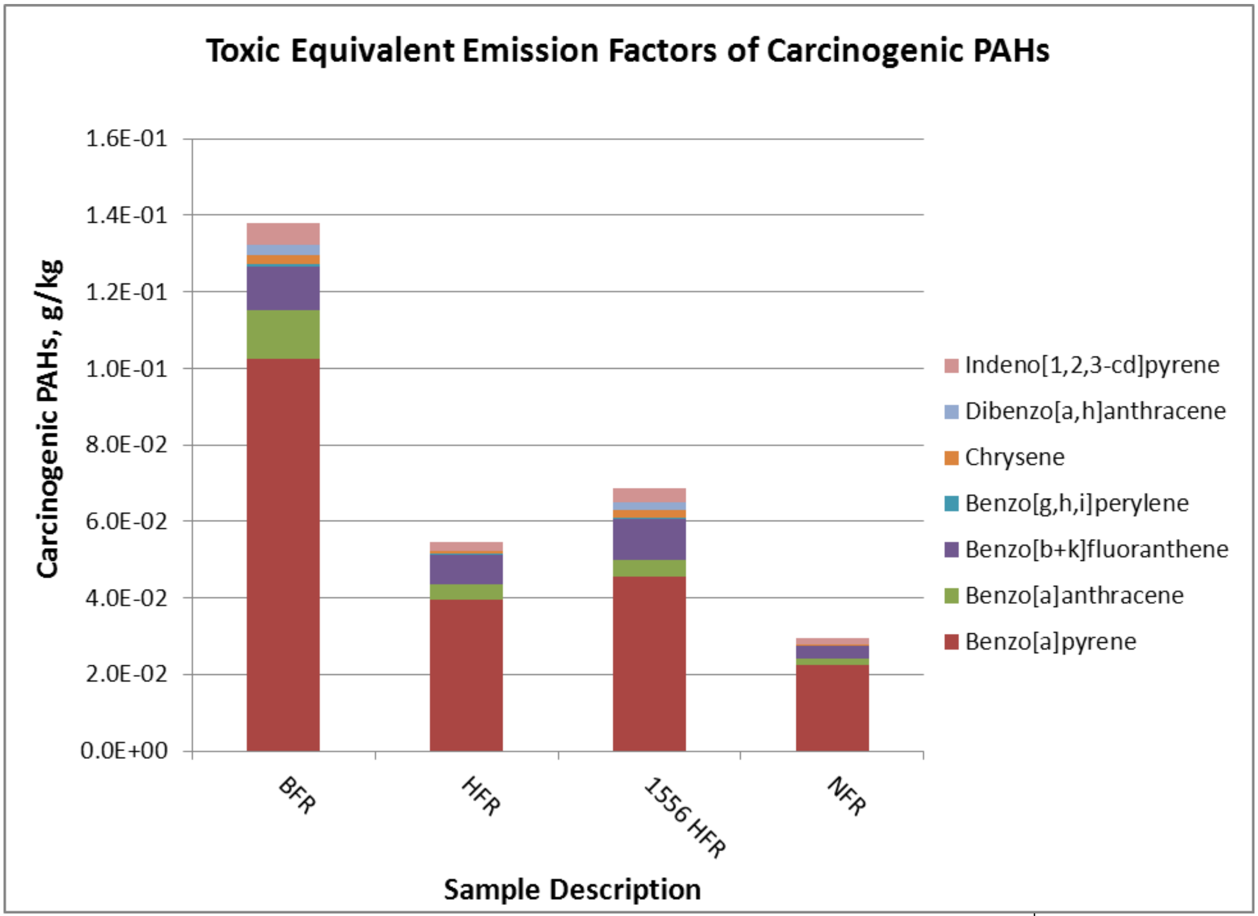

Figure 4-8. Toxic Equivalent Emission Factors of Carcinogenic PAHs from EPA List of 16‡ Priority PAHs Compared at 50 kW/m^2 Conditions
‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

Table 4-6. PAH Emission Factors from EPA List of 16‡ Priority PAHs for BFR and NFR at 50 and 100 kW/m^2

Analyte	Sample Description - Heat flux (kW/m^2)					
	BFR - 50	**BFR - 100**	**BFR + P - 50**	**BFR + PHF - 50**	**NFR - 50***	**NFR - 100**
	Emission Factors, g/kg					
Naphthalene	4.3E-01	2.1E-02	3.1E-02	2.5E-02	4.1E-03	7.7E-03
Acenaphthylene	2.6E+00	2.9E+00	1.8E+00	1.7E+00	1.9E-01	2.9E-01
Acenaphthene	1.1E-02	5.4E-03	6.3E-03	5.4E-03	0.0E+00	0.0E+00
Fluorene	2.3E-01	2.1E-01	1.8E-01	1.8E-01	7.2E-02	2.7E-01
Phenanthrene	8.0E-01	9.6E-01	8.3E-01	8.2E-01	1.2E-01	6.1E-01
Anthracene	8.7E-02	1.0E-01	9.3E-02	9.4E-02	4.9E-02	2.2E-01
Fluoranthene	1.6E-01	1.5E-01	1.7E-01	1.5E-01	2.7E-02	1.1E-01
Pyrene	1.4E-01	1.7E-01	1.5E-01	1.1E-01	4.3E-02	1.7E-01
Benz[*a*]anthracene	1.3E-01	7.3E-02	1.2E-01	9.9E-02	1.6E-02	3.4E-02
Chrysene	2.6E-01	2.2E-01	2.7E-01	2.5E-01	3.3E-02	8.2E-02
Benzo[*b*+*k*]fluoranthene	1.2E-01	9.4E-02	1.1E-01	1.1E-01	3.3E-02	5.5E-02
Benzo[*a*]pyrene	1.0E-01	9.2E-02	8.6E-02	7.2E-02	2.3E-02	4.0E-02
Indeno[*1,2,3-cd*]pyrene	5.6E-02	4.5E-02	5.3E-02	4.0E-02	1.4E-02	3.6E-02

Analyte	Sample Description - Heat flux (kW/m^2)					
	BFR - 50	BFR - 100	BFR + P - 50	BFR + PHF - 50	NFR - 50*	NFR - 100
	Emission Factors, g/kg					
Dibenz[*a*,*h*]anthracene	2.6E-02	2.7E-02	2.5E-02	2.1E-02	0.0E+00	0.0E+00
Benzo[*g*,*h*,*i*]perylene	4.8E-02	3.7E-02	4.7E-02	2.7E-02	8.2E-03	2.7E-02
Total 16 EPA PAHs	**5.22E+00**	**5.08E+00**	**3.93E+00**	**3.69E+00**	**6.24E-01**	**1.95E+00**

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

*From a single run

Table 4-7. PAH Emission Factors from EPA List of 16‡ Priority PAHs for HFR and 1556 HFR at 50 and 100 kW/m^2

Analyte	Sample Description - Heat flux (kW/m^2)						
	HFR - 50*	HFR - 100	HFR + P - 50	HFR + PHF - 50	1556 HFR - 50	1556 HFR + P - 50	1556 HFR + PHF - 50
	Emission Factors, g/kg						
Naphthalene	7.9E-03	8.4E-03	6.7E-03	6.7E-03	1.9E-02	6.3E-03	1.6E-02
Acenaphthylene	5.1E-01	5.5E-01	7.7E-01	6.2E-01	9.6E-01	7.4E-01	7.1E-01
Acenaphthene	7.9E-03	3.6E-03	1.8E-03	6.7E-03	6.7E-03	0.0E+00	6.9E-03
Fluorene	1.9E-01	1.6E-01	1.7E-01	2.4E-01	4.8E-01	1.9E-01	3.1E-01
Phenanthrene	4.5E-01	3.6E-01	4.7E-01	3.4E-01	6.0E-01	5.4E-01	4.2E-01
Anthracene	1.1E-01	9.3E-02	9.8E-02	8.6E-02	1.3E-01	9.7E-02	8.7E-02
Fluoranthene	8.7E-02	7.5E-02	1.0E-01	1.0E-01	1.4E-01	1.3E-01	1.3E-01
Pyrene	1.2E-01	1.1E-01	1.0E-01	7.8E-02	1.2E-01	8.3E-02	7.9E-02
Benz[*a*]anthracene	3.6E-02	1.9E-02	4.0E-02	3.6E-02	5.0E-02	5.5E-02	4.2E-02
Chrysene	7.9E-02	4.1E-02	1.3E-01	9.6E-02	2.0E-01	1.9E-01	1.4E-01
Benzo[*b*+*k*]fluoranthene	7.9E-02	3.1E-02	6.7E-02	6.4E-02	1.1E-01	8.6E-02	8.1E-02
Benzo[*a*]pyrene	4.0E-02	2.0E-02	4.2E-02	3.4E-02	4.5E-02	5.3E-02	4.1E-02
Indeno[*1*,*2*,*3*-*cd*]pyrene	2.4E-02	2.6E-02	2.4E-02	1.8E-02	3.7E-02	3.1E-02	2.4E-02
Dibenz[*a*,*h*]anthracene	0.0E+00	0.0E+00	1.2E-02	1.0E-02	2.2E-02	1.8E-02	1.3E-02
Benzo[*g*,*h*,*i*]perylene	2.4E-02	1.6E-02	1.5E-02	1.2E-02	1.9E-02	1.6E-02	1.2E-02
Total 16 EPA PAHs	**1.74E+00**	**1.51E+00**	**2.04E+00**	**1.75E+00**	**2.93E+00**	**2.24E+00**	**2.11E+00**

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

*From a single run

Table 4-8. Toxic Equivalent Emission Factors of Carcinogenic PAHs from EPA List of 16‡ Priority PAHs

Carcinogenic -PAHs	Toxic Equivalency Factor (TEF)	Toxic Equivalent Emission Factors of Carcinogenic PAHs (g/kg)			
		BFR	HFR	1556 HFR	NFR
Benzo[*a*]pyrene	1	1.0E-01	4.0E-02	4.5E-02	2.3E-02
Benzo[*a*]anthracene	0.1	1.3E-02	4.0E-03	4.5E-03	1.6E-03
Benzo[*b*+*k*]fluoranthene	0.1	1.2E-02	7.9E-03	1.1E-02	3.3E-03
Benzo[*g*,*h*,*i*]perylene	0.01	4.8E-04	2.4E-04	1.9E-04	8.2E-05
Chrysene	0.01	2.6E-03	7.9E-04	2.0E-03	3.3E-04
Dibenzo[*a*,*h*]anthracene	0.1	2.6E-03	0.0E+00	2.2E-03	0.0E+00
Indeno[*1*,*2*,*3*-*cd*]pyrene	0.1	5.6E-03	2.4E-03	3.7E-03	1.4E-03

‡Benzo[b]fluoranthene and benzo[k]fluoranthene are reported together

Although attempts were also made to determine presence of other chlorinated benzenes/phenols known to be PCDD/Fs precursors, none were detected at the sample concentrations analyzed for PAHs. No significant presence of chlorobenzenes and phenols detected in the laminate burns is a likely indicator of a negligible presence of chlorinated dioxins under the conditions explored in this study. However, the absence of PCDD/Fs cannot be conclusively stated without further analysis of more concentrated samples or attempts to analyze extracts for PCDD/Fs disregarding the previously discussed issues related to the absence of the chlorinated pre-sampling surrogates.

Scanning for organophosphorus was also done because it was believed that the non-halogenated flame retardants present in the samples were phosphorus-based. The detection of organophosphorus emissions would indicate the presence of a vapor phase flame retardant while the detection of no organophosphorus emissions would indicate the presence of a condensed phase flame retardant. The organophosphorous compounds detected in this study are given in Table 4-9. As Table 4-9 shows, different compounds were detected from the repeat burn of the same laminate. The environmental and health effects of the compounds detected are not evaluated in this report to explain their impact. From a flame retardant perspective, some of the compounds fit with known flame retardant chemistry while others are likely post-combustion reaction products or reactions between the phosphorus flame retardant and parts of the circuit board. For example, the phosphorous compounds with silicon in their chemical structure are likely present due to reactions between organophosphorus and e-glass during burning. The presence of any halogen-phosphorus compounds is likely due to reaction between halogen and organophosphorus during burning. Other organophosphorus compounds present that contain phosphonic or phosphinic acids are decomposition products of known phosphorus flame retardants, especially compounds containing phenyl groups. However, it should be recognized that the exact phosphorus flame retardant used in these systems was not reported to UDRI, leaving the interpretation of the data based upon information in open literature for phosphorus flame retardants. Combustion chemistry is complex, especially when many components are present, and the list of compounds detected is not surprising.

Table 4-9. Organophosphorous Compounds Detected

Laminate Description	Organophosphorous Compounds Detected	Area %
BFR -50	1-Ethyl-1-hydridotetrachlorocyclotriphosphazene	0.04
BFR -50	Silanol, trimethyl-, pyrophosphate	0.51
BFR + P -50	Phosphonic acid, methylenebis-, tetrakis(trimethylsilyl) ester	0.17
	O,O'-(2,2'-Biphenylylene)thiophosphoric acid	0.38
BFR + P -50	Bis(4-methoxyphenyl)phosphinic acid	0.1
BFR + PHF-50	Silanol, trimethyl-, pyrophosphate(4:1)	0.08
	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.61
	4-Phosphaspiro[2.4]hept-5-ene, 4-methyl-5,6-diphenyl-	0.15
	Bis(4-methoxyphenyl)phosphinic acid	0.15
BFR + PHF-50	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.23
BFR -100	Ethylphosphonic acid, bis(tert-butyldimethylsilyl) ester	8.33
BFR -100	Methylenebis(phosphonic acid), tetrakis(3-hexenyl) ester	0.29
HFR +P-50	Phosphonic acid, phenyl-, diethyl ester	0.25
HFR + PHF-50	(2-Bromo-3-methylphenyl) diphenylphosphine	0.34
HFR + PHF-50	Phosphine imide, P,P,P-triphenyl-	0.3
1556 + P -50	Phosphorane, 11H-benzo[a]fluoren-1-ylidenetriphenyl-	0.43
	1-Phosphacyclopent-2-ene, 1-methyl -5-methylene-2,3-diphenyl-	0.53
1556 + PHF-50	Phosphine imide, P,P,P-triphenyl-	0.21

4.7 Heat Release (Flammability) Results

The flammability data for the laminate samples and laminates + component powders are shown in Appendix A. Since material flammability/fire safety was not the primary focus of this study, it is not a primary focus of the Results and Discussion section. Instead, suggestions are provided on how the heat release results should and should not be interpreted and used.

The circuit board samples in this report are likely formulated to pass a small flame test, such as UL-94 V-0/-1/-2 (ASTM D3801), or a glow wire test (ASTM D6194) that mimics a short circuit ignition scenario. The cone calorimeter used in this report represents a well-ventilated fire scenario when it is run at a flow of 24 L/s as per the ASTM E1354 method. It better represents a larger fire source and not the small ignition source typically seen in electronic circuit boards. In this report, the cone calorimeter experiments were run at a lower flow rate of 15 L/s, which would roughly simulate open burn type conditions, not an intense well ventilated fire. Further, where ASTM D3801 uses a small flame source, the cone calorimeter uses a radiant heater, which in this case was set to heat fluxes of 50 and 100 kW/m^2 and represent a medium sized and a very large scale fire, respectively. The measurement of heat release from materials that were not designed to protect against robust heat sources like that of the cone calorimeter is a limitation of this study. It should not be used to infer the fire safety of the products in their respective scenarios. Each fire test used for regulating flame retardant materials is tailored for a specific fire risk scenario; the standards are not interchangeable. Therefore, the cone calorimeter data in this study is best used to understand how much heat an object gives off when burned in a situation where it is well ventilated and a robust heat source is present. With this in mind, heat release rate and smoke data from the cone calorimeter testing of circuit boards can be used to better understand:

- Heat output from the burning material when properly disposed of (100 kW/m^2 heat flux conditions) to know if the laminate gives off enough heat to run the incinerator cleanly.
- Heat output if e-waste was to be used for waste-to-energy processes (how much energy would be generated by the burning of e-waste).
- Relative rankings on flame retardant performance *outside* the regulatory test scenario for which it was designed. Specifically, cone calorimeter measures can inform how the materials would contribute to a larger fire event (server room fire, house fire) when set afire by another object in the same room. The lower the heat release of the material, the less likely it will contribute negatively to a large fire event, or, spread fire should it be exposed to heat and flame.

While the cone calorimeter data can be useful, care should be taken when using it for the selection of fire safe materials, or in the case of this report, figuring out which flame retardant chemistry (brominated or non-halogenated) is appropriate for a particular need. Cone calorimeter data can guide selections, but each material scientist and engineer will need to look closely at the fire standards to decide what aspect of fire performance certain materials must meet.

Although cone calorimeter measurements can give insight into heat output and comparative flame retardant performance, there are conclusions that cannot be made with the flammability/heat release data in this report:

- The measured heat release of each of the system does not infer that any one material is safer than another from a fire safety perspective. Since the cone calorimeter measures flammability in a different way than other regulatory tests, a low heat release in the cone calorimeter does not ensure a “pass” result in a regulatory test. A lower peak HRR would mean that the burning laminate would be less likely to ignite other nearby objects though. A lower total HR would indicate that if the burning laminate was fully burned, it would contribute less total heat (fuel) to the overall fire.
- Smoke release in the cone calorimeter is very much a function of the combustion conditions used in the test. Smoke release may be more intense or less intense under different ventilation conditions and the results cannot be used to infer that a particular material will be better or worse than another in a different flaming combustion configuration/scenario. Smoke release in the cone calorimeter is very different than smoke release from a full high heat flux fire and is also very different than smoke release from a small flame ignition source.
- Cone calorimeter data has a known % error of ±10%.

With the above caveats in mind, the following trends are observed in Table 4-10 and Table 4-11:

- At a heat flux of 50 kW/m^2, the flame retardant systems show lower peak heat release when compared to the non-flame retardant systems. The non-halogenated “1556 HFR” sample shows the lowest flammability overall but also has a lower amount of total mass lost, suggesting that it either has more non-combustible mass present or is a more robust char forming flame retardant system.

- The addition of component powders generally increased total heat release and had mixed effects on peak HRR.
- At a heat flux of 100 kW/m^2, only the brominated flame retardant continues to lower heat release (peak HRR and total HR) versus the non-flame retardant control. The non-halogenated system gives heat release roughly equal to, or slightly higher, than the non-flame retardant system.

Table 4-10. Heat Release Summary for Laminates and Laminates + Component Powders Tested at 50 kW/m^2

Sample Description - Heat Flux (50 kW/m^2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m^2)	Average HRR (kW/m^2)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	MARHE (kW/m^2)
BFR -1	0.49	11	279.0	65.31	37.2	4.4	485.2	115.6
BFR -2	0.49	10	272.4	64.23	39.8	4.8	496.9	114.2
BFR -3	0.50	10	296.5	91.31	37.5	4.8	455.2	146.8
BFR + P -1	0.49	9	280.2	81.29	29.3	6.9	719.9	127.7
BFR + P -2	0.48	8	265.0	79.41	28.8	6.9	698.5	116.3
BFR + P -3	0.49	14	255.7	79.94	27.9	6.6	657.0	105.9
BFR + PHF -1	0.48	12	279.3	83.44	25.2	6.8	467.1	111.7
BFR + PHF -2	0.48	18	331.4	88.70	25.1	6.9	446.5	107.5
BFR + PHF -3	0.48	14	266.8	81.37	24.9	6.9	490.8	108.4
NFR -1	0.43	11	406.1	77.77	32.3	5.8	228.3	130.0
NFR -2	0.41	11	391.6	87.52	28.4	6.1	199.0	139.4
NFR -3	0.44	12	445.9	88.69	34.9	6.5	238.8	140.8
HFR -1	0.57	12	406.7	98.15	35.8	7.8	240.2	141.4
HFR -2	0.56	15	292.1	84.51	32.3	6.7	237.5	106.9
HFR -3	0.58	17	368.5	94.59	34.2	7.3	274.7	124.7
HFR + P -1	0.56	10	267.4	88.64	25.0	8.2	451.2	116.1
HFR + P -2	0.58	8	278.9	102.55	25.9	9.6	461.4	139.8
HFR + P- 3	0.58	14	303.5	102.61	25.6	9.2	403.0	128.4
HFR+ PHF -1	0.58	21	343.0	111.98	25.1	9.8	330.9	128.4
HFR + PHF -2	0.57	31	294.0	96.43	21.5	7.8	372.5	92.4
HFR + PHF -3	0.56	26	271.1	86.55	22.5	8.0	356.9	98.5
1556 HFR -1	0.46	14	181.2	55.56	27.2	4.2	270.5	76.0
1556 HFR -2	0.45	24	205.9	50.88	23.0	3.6	232.1	60.7
1556 HFR -3	0.46	16	230.9	63.06	25.3	4.6	236.4	84.1
1556 HFR + P -1	0.46	12	165.7	73.22	23.3	6.6	400.4	93.1
1556 HFR + P-2	0.46	9	185.9	68.54	20.9	6.1	382.6	92.3
1556 HFR + P-3	0.45	9	165.8	71.18	22.8	6.6	409.3	92.2
1556 HFR +PHF -1	0.45	18	196.7	76.26	20.0	6.4	293.6	88.3
1556 HFR + PHF-2	0.46	22	209.4	83.15	20.4	7.1	324.0	88.6
1556 HFR +PHF -3	0.46	22	220.6	81.50	20.5	6.5	310.1	84.4

Table 4-11. Heat Release Summary for Laminates and Laminates + Component Powders Tested at 100 kW/m^2

Sample Description - Heat Flux (100 kW/m2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m^2)	Average HRR (kW/m^2)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	MARHE (kW/m^2)
BFR -1	0.41	3	226.7	55.5	41.1	4.5	475.6	128.5
BFR -2	0.42	5	390.6	80.4	45.8	5.7	451.0	180.2
BFR -3	0.40	3	356.8	77.0	45.3	5.4	392.7	189.4
NFR -1	0.32	3	356.4	79.7	36.5	5.3	194.6	188.4
NFR -2	0.35	4	490.5	94.5	38.9	6.6	230.1	201.3
NFR -3	0.34	4	387.5	70.8	37.5	5.0	219.5	152.5
HFR -1	0.49	6	494.7	104.0	38.6	7.4	231.4	205.4
HFR -2	0.48	6	495.2	104.9	35.8	7.5	237.5	215.9
HFR -3	0.49	5	367.1	120.0	40.5	10.2	325.6	200.5

5 Conclusions

While the cone calorimeter is a useful instrument for measuring flammability from a fire safety perspective, the use of the cone calorimeter in this study was as a combustion science tool. Heat fluxes plus a lower flow rate were chosen to represent potential open burn (50 kW/m^2) and incineration for metal recovery (100 kW/m^2). The following general trends were observed:

50 kW/m^2 heat flux:
- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at higher levels than NFR sample.
- NFR: PAHs emitted at lowest levels compared to other samples.

100 kW/m^2 heat flux:
- BFR: PBDD/Fs emitted. PAHs emitted at higher levels compared to other samples.
- HFR: PAHs emitted at lowest levels compared to other samples.
- NFR: PAHs emitted at a level slightly lower than the BFR sample.

Effect of components on emissions:
- PBDD/Fs: PBDD/Fs were similar or lower than sample without components.
- PAHs: In general, presence of components reduced PAH emissions for BFR, were similar or slightly highly for HFR and were lower for 1556 HFR. The size of these differences varied depending on which PAHs were summarized (see section 4.6).
- PAH emissions and smoke release of laminates with low halogen components were slightly lower than standard components across all three difference laminates.

Smoke, PM, CO and CO_2 release:
- Smoke release was higher for BFR than HFR laminates. Smoke release was higher with components due to greater amount of material. PM generally had small differences between samples. There were negligible differences in CO release between samples. CO_2 release was

lowest for BFR but with small differences between samples. Results are complex and smoke/PM results do not always correlate.

The results of this report do not suggest that any one material is safer than another in regards to fire safety. The results do show that the flame retardants lower heat release under flaming combustion even at high heat fluxes.

Overall, the results clearly show that all of the samples generated combustion by-products other than CO_2 and water. The flame retardant samples in some cases generated more pollutants than the NFR samples, as one would expect since the flame retardants are inhibiting combustion. Any system that slows down flaming combustion will generate higher levels of smoke, CO, PM, and other incomplete combustion products. A flame retardant with a vapor phase mechanism (such as BFR) will generate more species than a flame retardant that uses a condensed phase mechanism (assumed to be the case of the phosphorus-based HFR system). It is important to look at flame retardant chemistry, flame retardant mechanism, polymer decomposition chemistry, and fire scenario (heat, ventilation) to determine what sorts of species may be formed during accidental fires (where flame retardants serve as passive protection) or intentional ones (proper and improper incineration).

The other major finding of this report is that the cone calorimeter was able to obtain a diverse amount of information about emissions from circuit boards. For the brominated laminate with halogenated components, the complexity of the emissions made them difficult to separate and identify but the results show that pollutants exist. Further work and separation science would be needed to achieve that higher level of data resolution with these particular samples.

Based upon the results in this report, users of flame retardants for circuit boards should realize that if PCBs or other e-waste is to be incinerated for precious metal recovery, it should be done properly with good incinerator control to address the pollutant emissions that will occur. Even non-flame retardant boards when incinerated improperly will release pollutants of concern, as was seen from the data in this report. Emissions may have been lower, but they were still present. The use of flame retardants is a technology compromise: it provides fire safety performance (thus lowering risk of short circuit ignitions in daily use) but will generate higher pollutants when incinerated improperly. Other environmental concerns may drive the selection of different flame retardant chemistry, but from emissions alone, such a decision cannot be made. With careful attention to polymer thermal decomposition chemistry and combustion science, it may be possible to generate a flame retardant in the future which provides fire protection *and* minimizes emissions/pollutants of concern during burning. If there is a desire to develop clean burning flame retardant materials, entirely different flame retardant chemistries must be developed. Otherwise, the safest solution to this problem is to recover precious metals via well controlled incineration with regulatory emissions controls in place as well as cost-effective methods of e-waste collection and disposal.

6 Acknowledgments

The authors wish to thank Kathleen Beljan, Mary Galaska, and Kathy Schenck of UDRI for their assistance with the cone calorimeter tests and Anne Chauvian and Saikumar Chalivendra for their initial support for the modified experimental design work. Barbara Wyrzvkowska-Ceradini and Craig Williams assisted with sample extraction, clean-up and analysis at EPA labs. Funding and materials for the project were provided by Albemarle, Boliden, BSEF, Chemtura, Clariant, Ciba Specialty Chemicals, Dell, Fujitsu-Siemens, Hewlett-Packard, IBM, ICL-IP America Inc., Intel, Isola, ITEQ, Matsushita Electric Industrial and Matsushita Electric Works, Nabeltec, Panasonic, Seagate, Sony, Supresta, & U.S. EPA.

7 Appendix A: Circuit Board Flammability Data

Along with emissions data, heat release information as per ASTM E1354 was also collected. This data is reported in below as a function of heat flux and samples tested. Observed fire behavior, final chars, and heat release rate curves are given. The data is presented for the purposes of completeness in this report. It does not infer any particular level of fire safety about the samples tested. Merely it shows what the measured heat release information was from these samples when tested at 15 L/sec exhaust flow in triplicate as per the ASTM methodology.

In the section below, BFR indicates a brominated flame retardant system being tested, while HF indicates halogen-free flame retardant and NFR indicates that the sample had no flame retardant present. Component blends are identified as “Comp”, meaning a component blend where halogen was present in the component blend powder, and as “HF Comp” meaning the mostly halogen-free component blend was used.

Heat Release Rate-50 kW/m^2

Table 7-1. Heat Release Rate Data (50 kW/m^2)

Sample Description - Heat Flux (50 kW/m^2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m^2)	Time to Peak HRR (s)	Average HRR (kW/m^2)	Starting Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m^2)	FIGRA
BFR -1	0.5	11	279	20	65	10.5	3.9	37.2	4.4	485	15.14	116	13.95
BFR -2	0.5	10	272	20	64	10.8	4.3	39.8	4.8	497	11.21	114	13.62
BFR -3	0.5	10	296	25	91	10.4	3.9	37.5	4.8	455	17.58	147	11.86
BFR + P -1	0.5	9	280	30	81	20.5	6.0	29.3	6.9	720	11.92	128	9.34
BFR + P -2	0.5	8	265	35	79	20.5	5.9	28.8	6.9	699	11.71	116	7.57
BFR + P -3	0.5	14	256	34	80	20.4	5.7	27.9	6.6	657	11.50	106	7.52
BFR + PHF -1	0.5	12	279	33	83	20.3	5.1	25.2	6.8	467	13.09	112	8.46
BFR + PHF -2	0.5	18	331	37	89	20.3	5.1	25.1	6.9	447	13.39	108	8.96
BFR + PHF -3	0.5	14	267	32	81	20.5	5.1	24.9	6.9	491	13.14	108	8.34
NFR -1	0.4	11	406	28	78	9.3	3.0	32.3	5.8	228	18.66	130	14.50
NFR -2	0.4	11	392	26	88	9.1	2.6	28.4	6.1	199	22.87	139	15.06
NFR -3	0.4	12	446	29	89	9.5	3.3	34.9	6.5	239	19.36	141	15.37
HFR -1	0.6	12	407	31	98	11.4	4.1	35.8	7.8	240	19.00	141	13.12
HFR -2	0.6	15	292	39	85	11.5	3.7	32.3	6.7	238	17.75	107	7.49
HFR -3	0.6	17	368	36	95	11.4	3.9	34.2	7.3	275	18.44	125	10.24
HFR + P -1	0.6	10	267	45	89	21.2	5.3	25.0	8.2	451	15.36	116	5.94
HFR + P -2	0.6	8	279	39	103	21.6	5.6	25.9	9.6	461	17.01	140	7.15
HFR + P- 3	0.6	14	304	41	103	21.5	5.5	25.6	9.2	403	16.50	128	7.40
HFR+ PHF -1	0.6	21	343	49	112	21.5	5.4	25.1	9.8	331	17.90	128	7.00
HFR + PHF -2	0.6	31	294	47	96	21.4	4.6	21.5	7.8	373	16.67	92	6.26
HFR + PHF -3	0.6	26	271	43	87	21.3	4.8	22.5	8.0	357	16.38	99	6.30
1556 HFR -1	0.5	14	181	32	56	10.7	2.9	27.2	4.2	271	14.16	76	5.66
1556 HFR -2	0.5	24	206	38	51	10.5	2.4	23.0	3.6	232	14.61	61	5.42
1556 HFR -3	0.5	16	231	30	63	10.7	2.7	25.3	4.6	236	16.38	84	7.70

Sample Description - Heat Flux (50 kW/m^2)	**Sample Thickness (mm)**	**Time to ignition (s)**	**Peak HRR (kW/m^2)**	**Time to Peak HRR (s)**	**Average HRR (kW/m^2)**	**Starting Mass (g)**	**Total Mass Loss (g)**	**Weight % Lost (%)**	**Total Heat Release (MJ/m^2)**	**Total smoke Release (m^2/m^2)**	**Avg. Effective Heat of Comb. (MJ/kg)**	**MARHE (kW/m^2)**	**FIGRA**
1556 HFR + P -1	0.5	12	166	49	73	20.6	4.8	23.3	6.6	400	13.56	93	3.38
1556 HFR + P-2	0.5	9	186	34	69	20.6	4.3	20.9	6.1	383	13.99	92	5.47
1556 HFR + P-3	0.5	9	166	45	71	20.6	4.7	22.8	6.6	409	13.86	92	3.69
1556 HFR +PHF -1	0.5	18	197	34	76	20.0	4.0	20.0	6.4	294	15.73	88	5.79
1556 HFR + PHF-2	0.5	22	209	39	83	20.6	4.2	20.4	7.1	324	16.49	89	5.37
1556 HFR +PHF -3	0.5	22	221	44	82	20.5	4.2	20.5	6.5	310	15.31	84	5.01

BFR Fire Behavior

Upon exposure to the cone heater, the sample began to smoke and make crackling sounds very quickly. It then burst into flame with orange, blue, and purple colors noted. The sample was noted to curl up some during burning with the 2nd sample curling and delaminating to a severe degree such that the cone heater shutters could not close at the end of the experiments. Heat release was reproducible (Figure 7-1) and the final chars (Figure 7-2) were blackened with copper plates noted. The sample where the shutters could not be closed is shown on the far left of Figure 7-2 where the surface char has be slowly burned away leaving behind just copper and fiberglass. So with sufficient heat and oxygen, eventually most of the carbon can be burned away/ consumed.

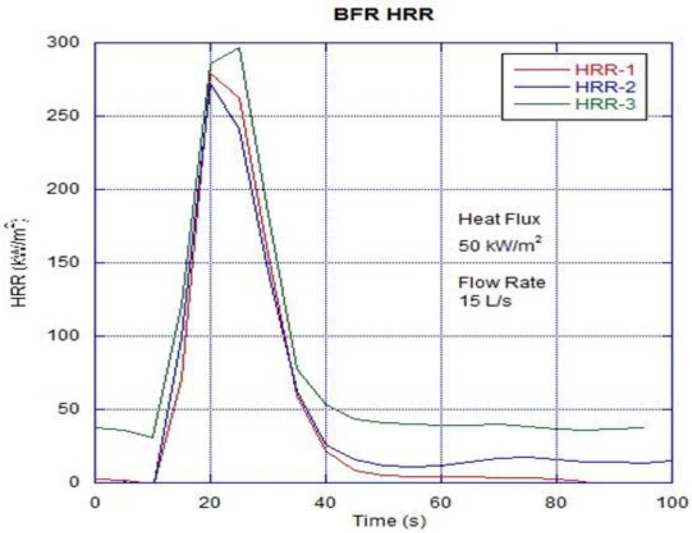

Figure 7-1. HRR for BFR Sample

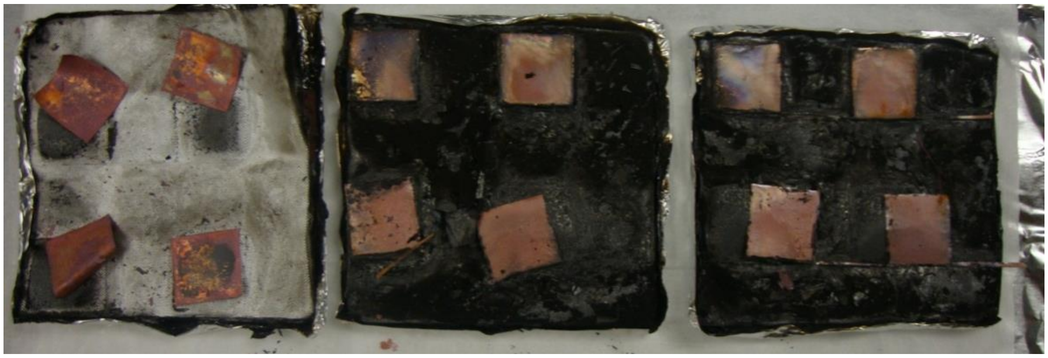

Figure 7-2. Final Chars for BFR Sample

BFR + P (populated halogen components)Fire Behavior

Fire behavior of this sample was the same as the BFR sample, but the flame colors were more muted. The component powder was also noted to spit and pop a bit, with occasional pieces of the powder leaving the aluminum foil holder. Heat release rates (Figure 7-3) were reproducible indicating that the powder did not inhibit burning behavior. Final chars (Figure 7-4) were black with yellowish-black powder on top.

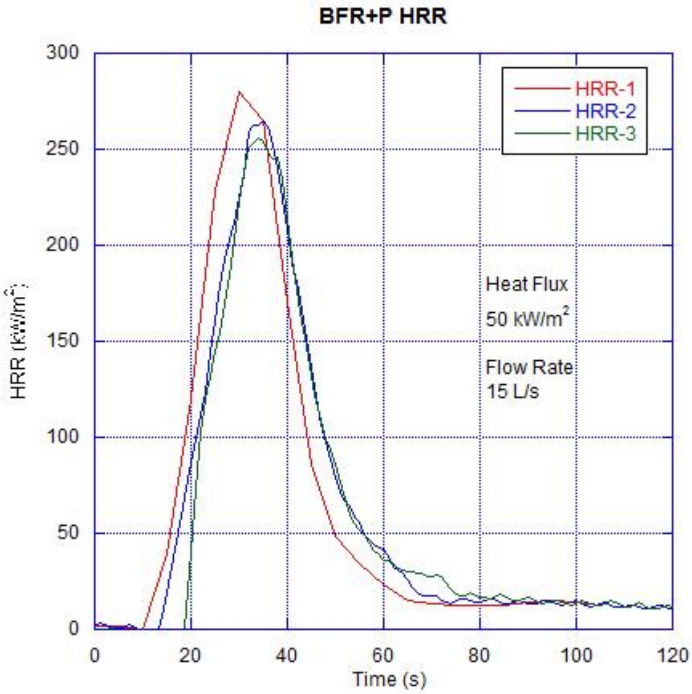

Figure 7-3. HRR for BFR + P Sample

Figure 7-4. Final Chars for BFR + P Sample

BFR + PHF(Populated halogen-free components)Fire Behavior

Upon exposure to the heater, the sample smoked and crackled, and then ignited on one side of the sample with the flames sweeping across the surface quickly. Flames were noted to be blue and purple in color, and the component powder had a tendency to crackle and bubble, suggesting the presence of thermoplastic material in the HF powder. HRR was fairly reproducible (Figure 7-5) although the 2nd sample (HRR-2) has a higher peak HRR and delayed time to ignition when compared to the other two samples. Final chars (Figure 7-5) were black with copper squares noted. From this observation the halogen-containing component powder does not flow (Figure 7-4) and may contain less thermoplastic material as opposed to the halogen-free component powder which appears to burn up more completely and leave less of a powdery residue.

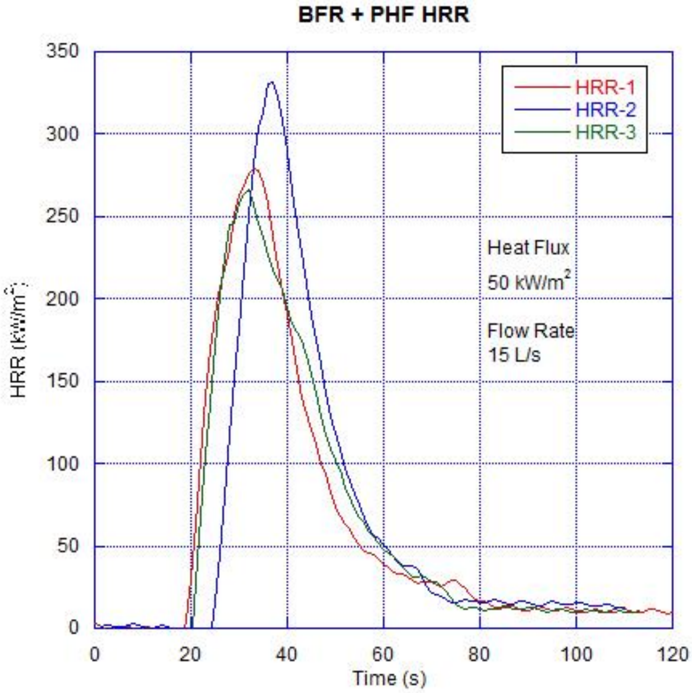

Figure 7-5. HRR for BFR + PHF Sample

Figure 7-6. Final Chars for BFR + PHF Sample

NFR Fire Behavior

Upon exposure the cone heater, the sample made a lot of crackling noises, and then began to smoke before quickly igniting. The sample curled quite a bit during burning such that the shutters could not be closed at the end of the experiment. Heat release (Figure 7-7) was very reproducible and the final chars (Figure 7-8) show just the copper and fiberglass as most of the residual carbon was burned away since the shutters would not close. Therefore any char which had self-extinguished during the test was slowly pyrolyzed away until the sample could be removed from the cone calorimeter.

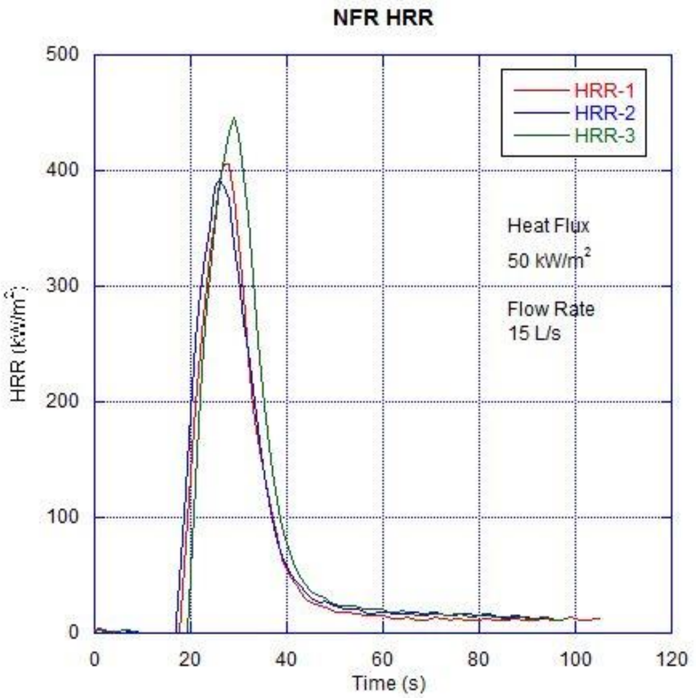

Figure 7-7. HRR for NFR Sample

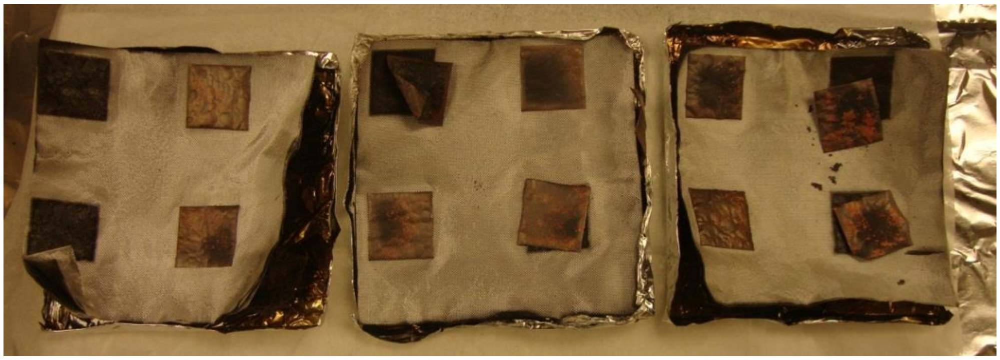

Figure 7-8. Final Chars for NFR Sample

HFR Fire Behavior

Upon exposure to the cone heater, the sample began to crackle and then smoke, followed by ignition. The sample burned with some white colors, suggesting the presence of a phosphorus-based flame retardant. The first sample curled during the test and the shutters could not be closed. Some scatter in the HRR was noted (Figure 7-9), especially in the peak HRR values. Final chars (Figure 7-10) in general show black-grey chars on the surface of the fiberglass, but some char is noted on the copper squares as well.

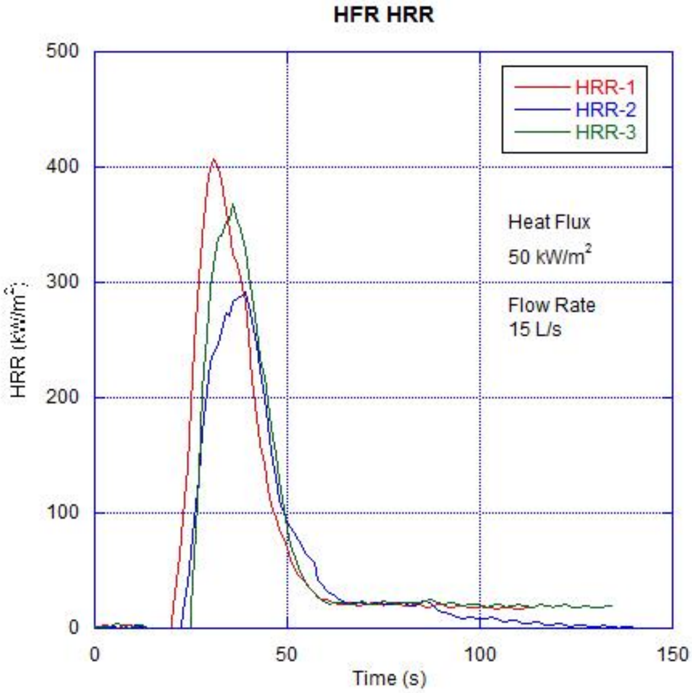

Figure 7-9. HRR for HFR Sample

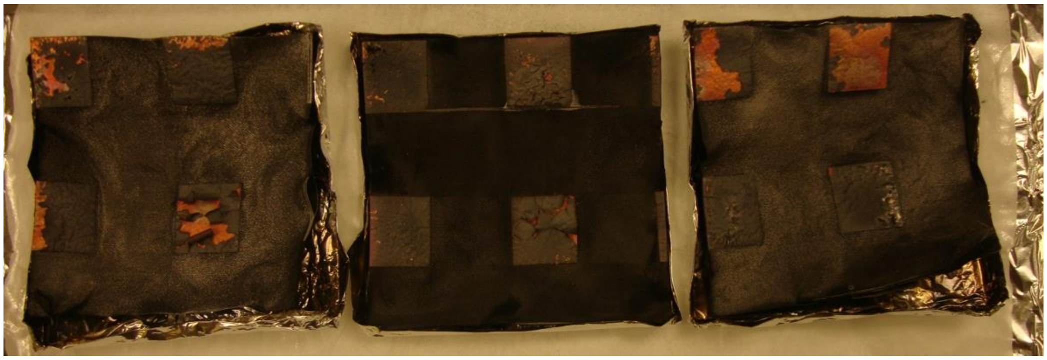

Figure 7-10. Final Chars for HFR Sample

HFR+ P (Comp) Fire Behavior

Upon exposure to the cone heater, the sample began to smoke right away, followed an ignition and some loud crackling noises. Some parts of the powder also spat out of sample surface during this burning behavior with some flames going out sideways from under the powder. Some blue flames were noted at the beginning and end of the test. The third sample tested had some curling and the shutters could not be closed at the end of the test. Heat release (Figure 7-11) showed some scatter in the peak HRR values, but the scatter was not severe. Final chars (Figure 7-12) were completely black and the powder is of a similar color, unlike the BFR sample above which had the same component powder but the powder char was of a different color at the end of the test (Figure 7-4). The curling observed for the 3rd sample can be seen in the middle of Figure 7-12.

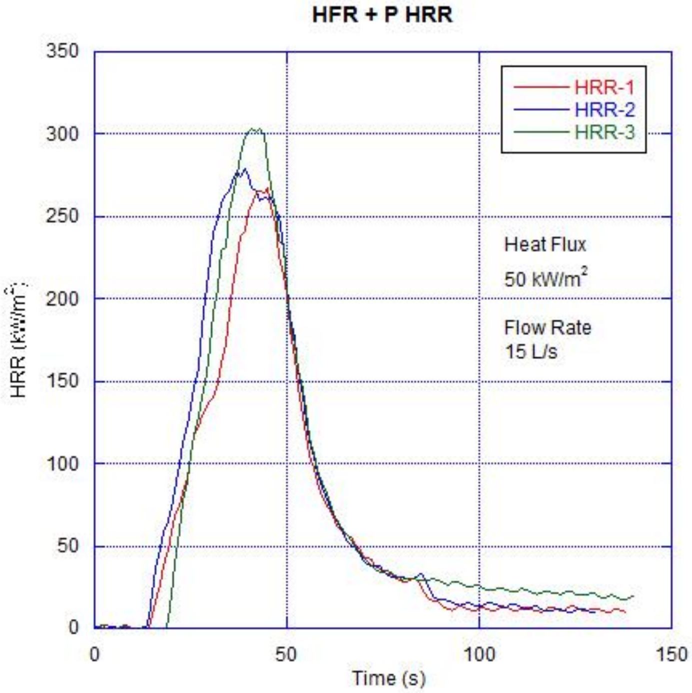

Figure 7-11. HRR for HFR + P Sample

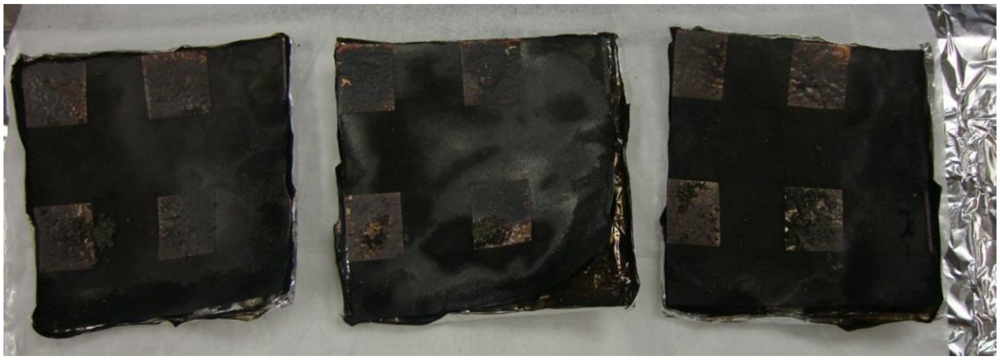

Figure 7-12. Final Chars for HFR + P Sample

HFR + PHF Fire Behavior

Fire behavior for this sample was similar to that of the sample above, except no blue colors were noted. All of the samples had a tendency to curl such that it was difficult to close the shutters at the end of the test. Loud crackling and popping was heard, but no bubbling seen this time as was observed for the BFR + PHF sample. HRR showed some scatter in the time to ignition and peak HRR values (Figure 7-13). Final chars (Figure 7-14) showed intact charred powder, but with more residual color noted. Some of the copper squares can be seen under the charred component powder.

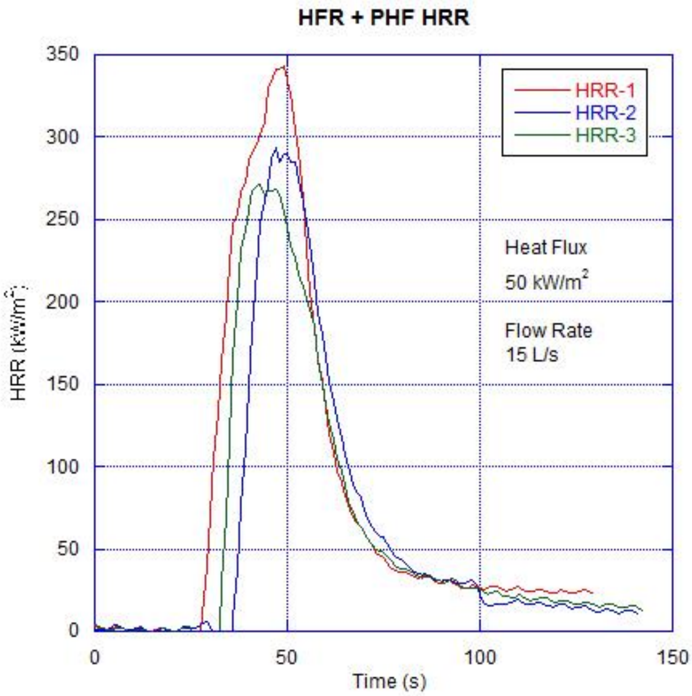

Figure 7-13. HRR for HFR + PHF Sample

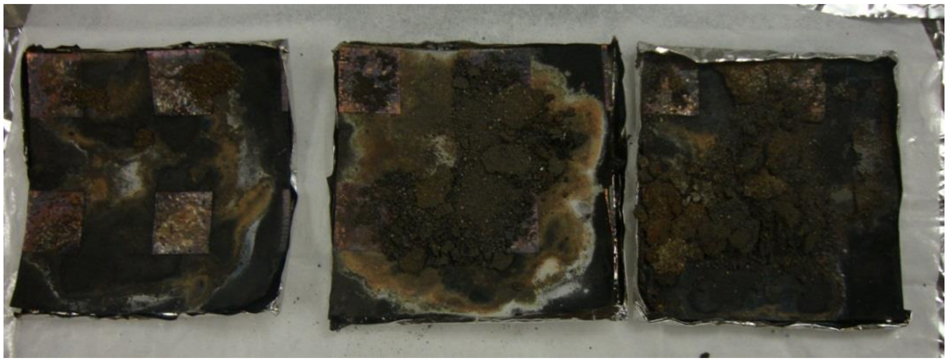

Figure 7-14. Final Chars for HFR + PHF Sample

1556 HFR Fire Behavior

Upon exposure to the cone heater, the sample was heard to crackle and pop, then smoke, then ignite. The sample had small flames which were not as sooty as those seen in previous samples. The sample also curled during burning, but flaked apart as it burned, suggesting the presence of a phenolic resin, or some sort of charring polymer. HRR (Figure 7-15) was not very reproducible for this sample, with notable variability in the peak HRR and time to peak HRR behavior. Final chars (Figure 7-16) are black and grey with regions of soot on the surface. Some of the copper squares have moved suggested they debonded from the surface during burning.

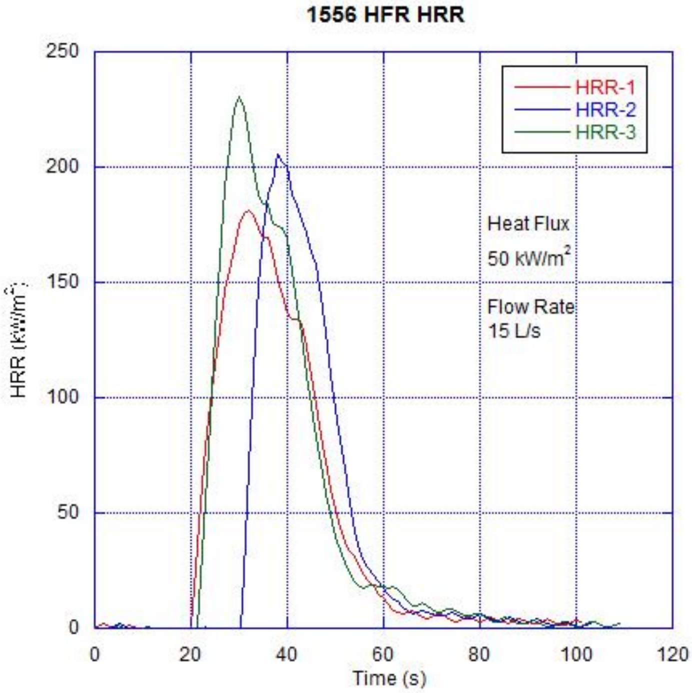

Figure 7-15. HRR for 1556 HFR Sample

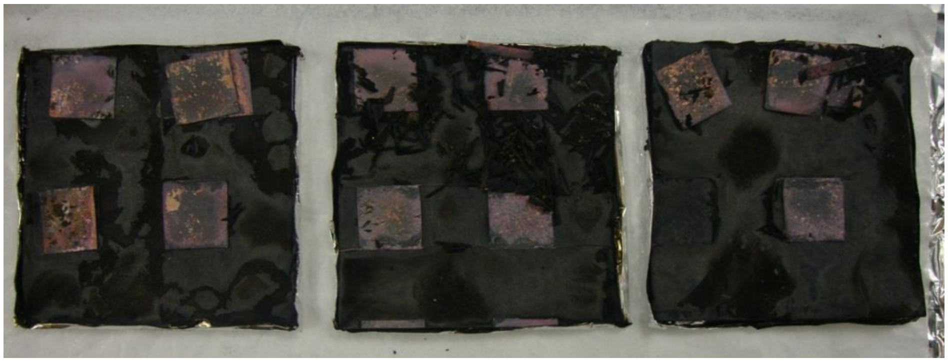

Figure 7-16. Final Chars for 1556 HFR Sample

1556 HFR+ P Fire Behavior

Fire behavior for this sample was similar to that of sample 1556 HFR, but some blue flames were noted as well. No real curling of the sample occurred when the powder was present, but some spitting of the component powder out of the sample holder was noted. HRR (Figure 7-16) was fairly reproducible, with only the 2nd sample (HRR-2) showing variability in the peak HRR and time to peak HRR. Final chars (Figure 7-17) were black underneath with copper squares and the powder was a dark yellow-green in color.

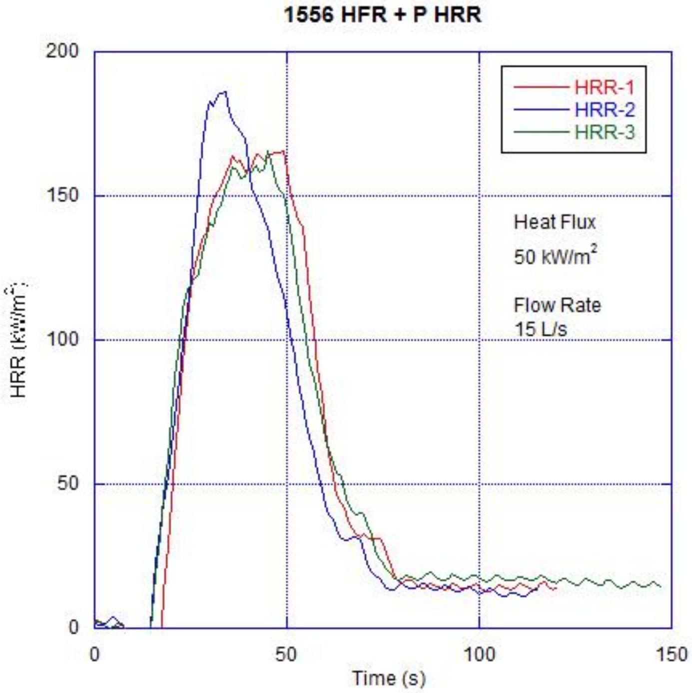

Figure 7-17. HRR for 1556 HFR + P Sample

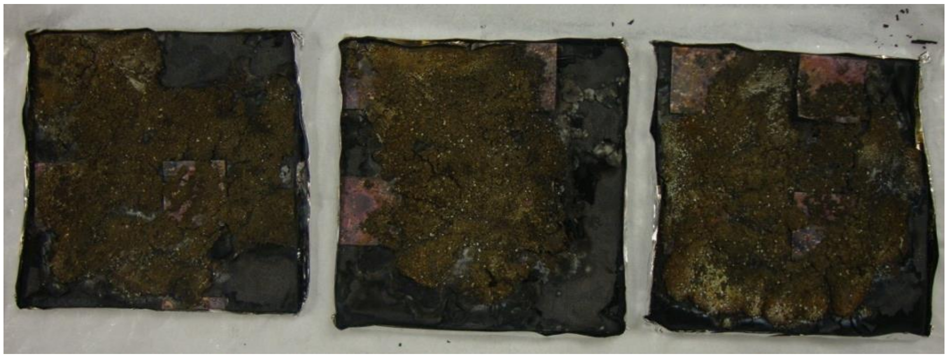

Figure 7-18. Final Char for 1556 HFR + P Sample

1556 HFR+ PHF Fire Behavior

Fire behavior for this sample was also similar to that of sample 1556 HFR, that some colors were seen in the flames toward the end of the test with some blue and blue/green colors noted. HRR (Figure 7-19) was reproducible and the final chars (Figure 7-20) were black and grey with the powder being mostly intact.

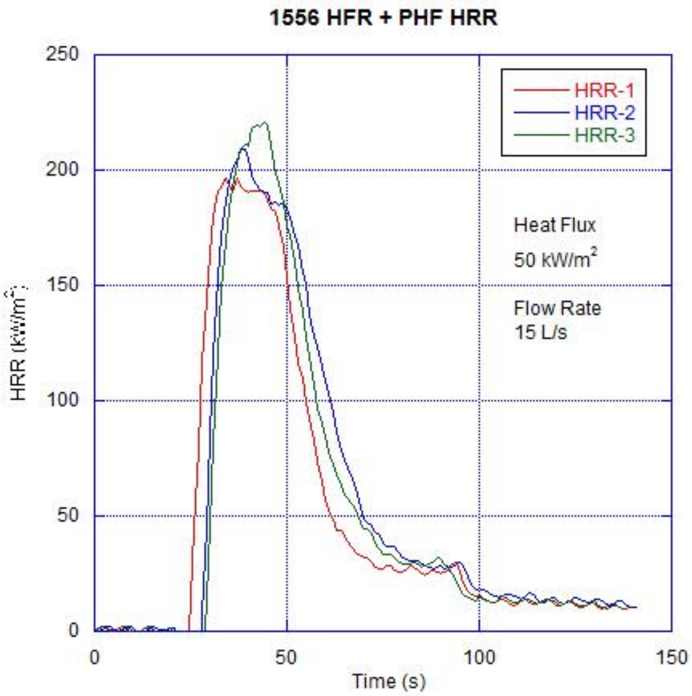

Figure 7-19. HRR for 1556 HFR + PHF Sample

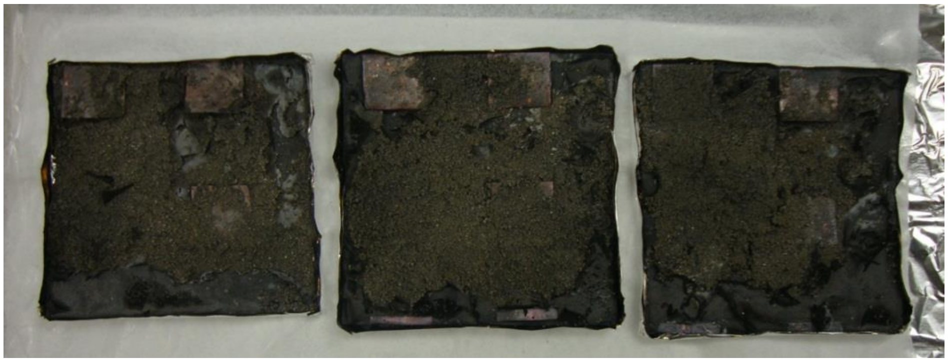

Figure 7-20. Final Chars for 1556 HFR + PHF Sample

Heat Flux-100 kW/m^2

Table 7-2. Heat Release Data (100 kW/m^2)

Sample Description - Heat Flux (50 kW/m^2)	Sample Thickness (mm)	Time to ignition (s)	Peak HRR (kW/m$^{2)}$	Time to Peak HRR (s)	Average HRR (kW/m^2)	Starting Mass (g)	Total Mass Loss (g)	Weight % Lost (%)	Total Heat Release (MJ/m^2)	Total smoke Release (m^2/m^2)	Avg. Effective Heat of Comb. (MJ/kg)	MARHE (kW/m^2)	FIGRA
BFR -1	0.4	3	227	15	56	10.2	4.2	41.1	4.5	476	11.05	129	15.11
BFR -2	0.4	5	391	15	80	10.7	4.9	45.8	5.7	451	11.58	180	26.04
BFR -3	0.4	3	357	15	77	10.4	4.7	45.3	5.4	393	11.72	189	23.79
NFR -1	0.3	3	356	15	80	8.8	3.2	36.5	5.3	195	17.75	188	23.76
NFR -2	0.4	4	490	15	94	9.5	3.7	38.9	6.6	230	18.37	201	32.70
NFR -3	0.3	4	387	15	71	8.8	3.3	37.5	5.0	220	15.91	153	25.83
HFR -1	0.5	6	495	20	104	10.9	4.2	38.6	7.4	231	18.49	205	24.74
HFR -2	0.5	6	495	20	105	11.2	4.0	35.8	7.5	238	20.75	216	24.76
HFR -3	0.5	5	367	25	120	14.1	5.7	40.5	10.2	326	17.95	201	14.68

BFR Fire Behavior

Upon exposure to the cone heater, the sample quickly began to smoke and crackle, and then ignited quickly. The flames were noted to be orange and blue in color. With some of the samples, smoke would shoot out the sides of the sample and escape the cone calorimeter exhaust ducting. Some of the samples also curled/deformed during testing. Heat release (Figure 7-21) showed some notable scatter in the peak HRR value for the 1st sample (HRR-1). The reasons for this scatter with the 1st sample are not clear at this time, but perhaps this sample had slightly less flammable epoxy mass than the other two samples tested. Final chars (Figure 7-22) were dark grey with exposed glass fiber and burned/damaged copper metal squares.

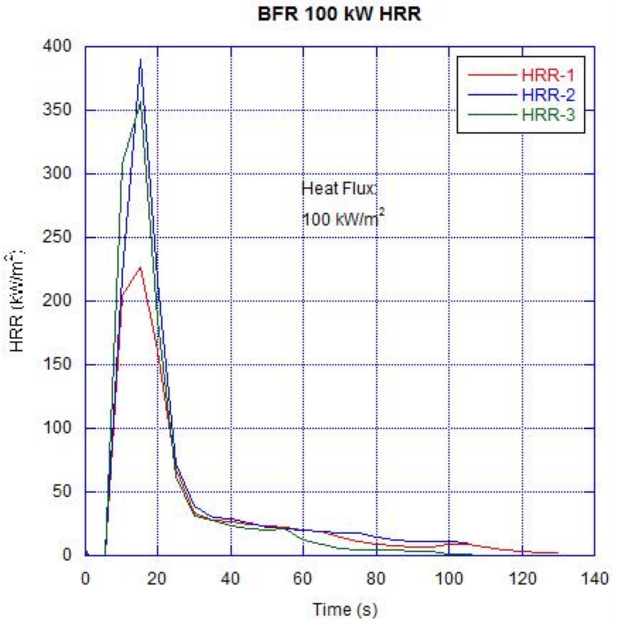

Figure 7-21. HRR for BFR Sample

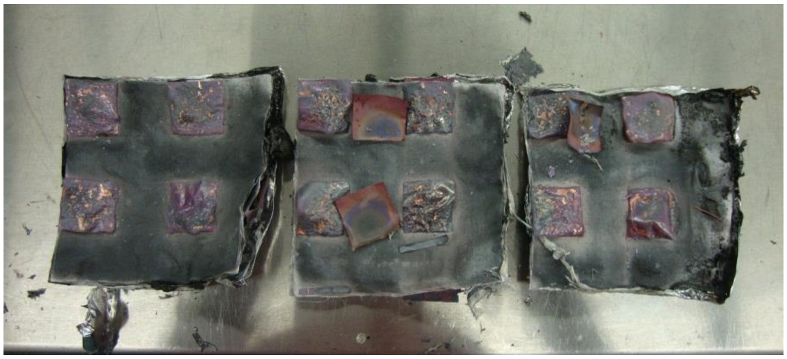

Figure 7-22. Final Chars for BFR Sample

NFR Fire Behavior

Fire behavior was identical to that of the BFR sample, except no blue colors in the flames were noted, the appeared to be more charring and soot generated during burning, and more curling/deformation was noted during burning. HRR was fairly reproducible (Figure 7-23) and the final chars (Figure 7-24) were blackened over most of the surface, including the copper metal squares.

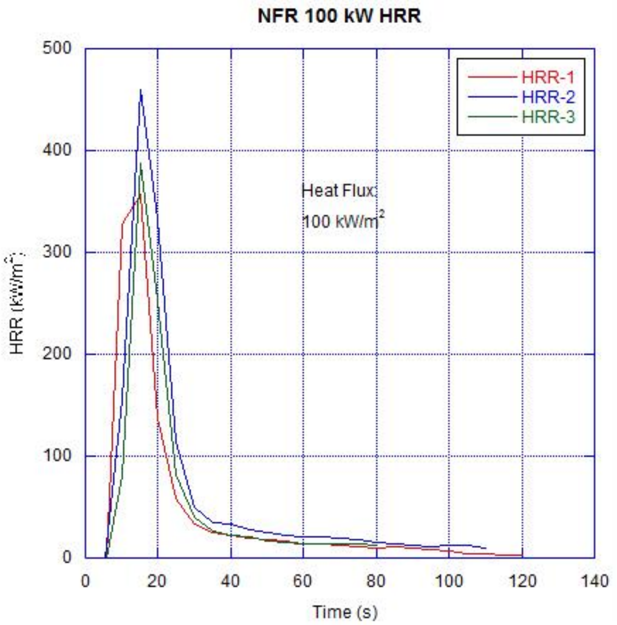

Figure 7-23. HRR for NFR Sample

Figure 7-24. Final Chars for NFR Sample

HFR Fire Behavior

Upon exposure to the heater, the sample began to smoke and crackle, with more of a whiter smoke noted prior to ignition. Some deformation during burning was noted, and the sample was noted to have a distinct smell to it when removed from the cone heater. HRR was reproducible for the 1st two samples (HRR-1, HRR-2), but the third sample (HRR-3) shows a lower peak HRR and a bit of delay in time to peak HRR (Figure 7-25). Again, reasons for this difference are unclear at this time. Since some of the samples deformed greatly during testing, it was not possible to close the cone heater shutters at the end of the test and so the samples were exposed to additional heat at the end of the test after extinguishment which burned off additional surface char, yielding light grey specimens of bare glass fiber (Figure 7-26). One of the samples did not deform as much and the shutters could be closed, giving a specimen with more surface char (middle of Figure 7-26).

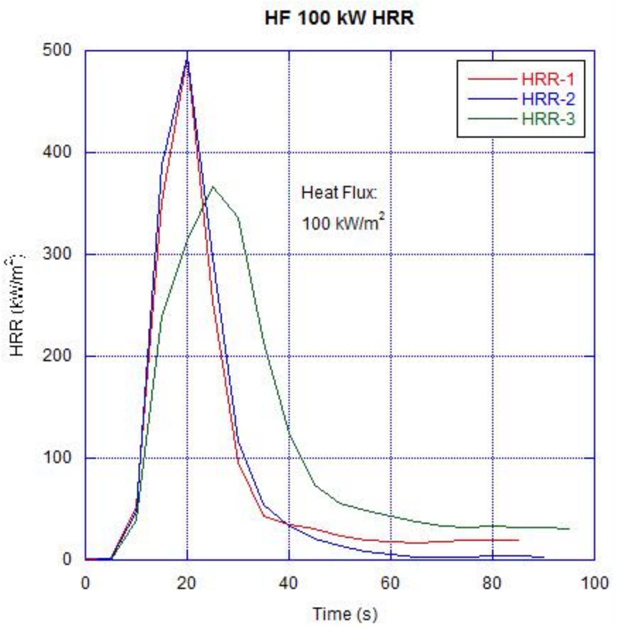

Figure 7-25. HRR for HFR Sample

Figure 7-26. Final Chars for HFR Sample

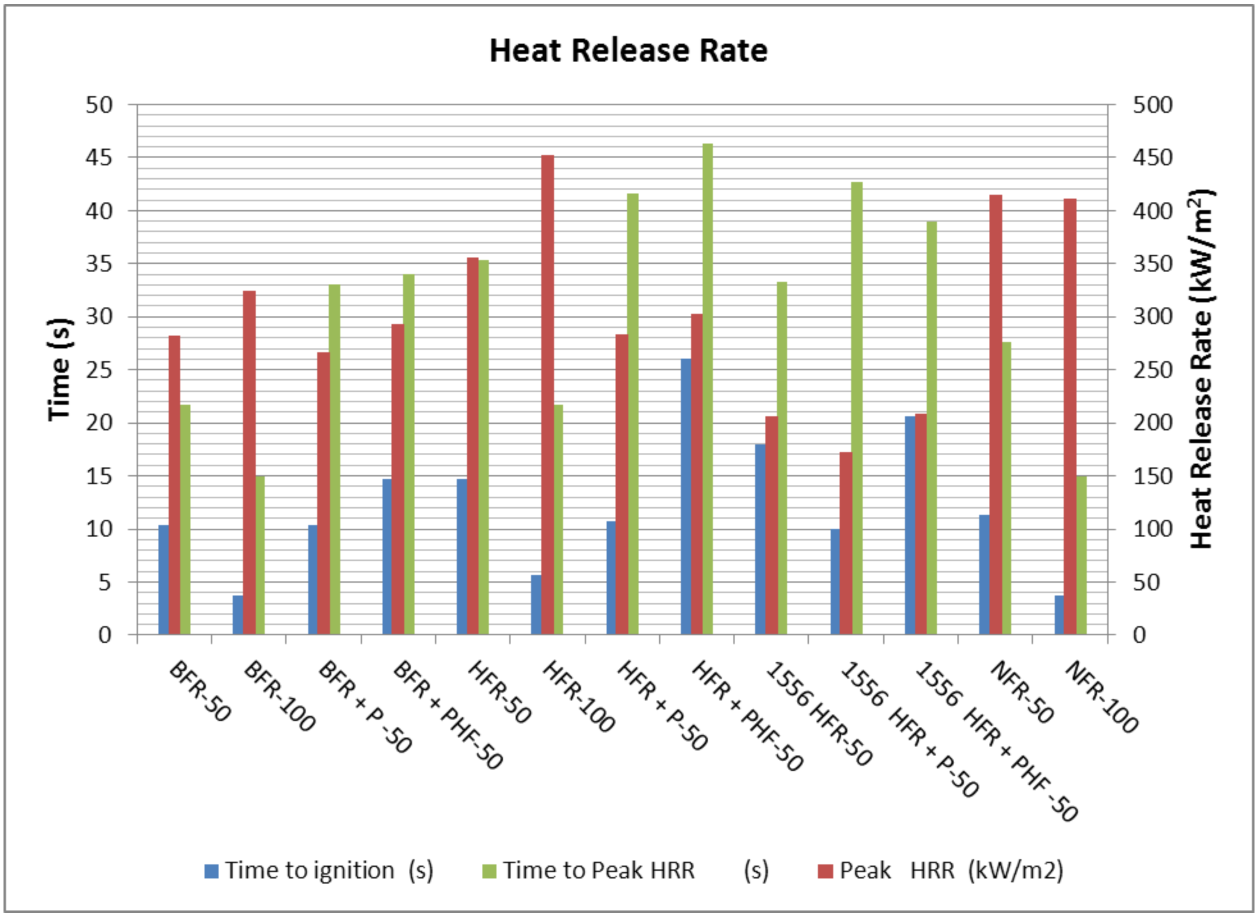

Figure 7-27. Heat Release Rate Plot

Overall Remarks on 50 kW/m^2 Heat Flux Sample Burning Behavior:

There are notable interactions between the component powder and the polymer decomposition chemistry going on as these samples burn. Brominated FR epoxy reacts differently with halogen-containing and halogen-free component powder, as does the halogen-free epoxy. The 1556 HFR sample also shows some differences when exposed to the two different powders, but not to as great a degree seen with the BFR and HF epoxy samples. The behavior of the HF comp powder is worth noting on here since in one case it showed bubbling but not in others. This may be due to a unique flame retardant reaction in the presence of brominated epoxy, but no obvious reason for this behavior can be given at this time.

The BFR samples, as expected, gave off lots of smoke and pyrolyzed some of the copper away in the form of copper halides, which were seen in the flames as blue colors. The HF samples showed some white colors indicating phosphorus release, but no blues until halogen-containing component powder was added, suggesting that less copper was pyrolyzed during burning. The 1556 HFR samples showed color in the presence of the halogenated powder, and surprisingly in the presence of the HF component powder as well, indicating the components again have an effect on metal pyrolysis/thermal reaction behavior.

Overall Remarks on Burning Behavior – 100 kW/m^2 Heat Flux:

At 100 kW/m^2 heat flux, the differences in fire behavior between the samples tested were minimal, but there were some differences noted in physical burning behavior which correlate to the fire behavior noted at 50 kW/m^2 heat flux. The brominated FR epoxy does give off more smoke and does inhibit combustion as expected, and the blue colors noted during burning are visual evidence of bromine reacting with copper under burning/pyrolysis conditions. The non-FR sample burns quickly and rapidly (as a sample with no flame retardant should), and the non-halogenated FR sample also shows physical fire behavior similar to that of the non-FR sample. The non-halogenated FR has an equally high effective heat of combustion to that of the non-FR sample which may just suggest that the flame retardant mechanism for this material has little effect at very high heat fluxes, or at least does not inhibit combustion as much at very high heat fluxes. Smoke release is slightly higher though, and so the non-halogenated FR sample is having some effect on combustion products even if no change in measured heat of combustion is observed.

8 Appendix B: Experimental Conditions

Table 8-1. Ambient Conditions during Cone Testing

Experiment #	Laminate Description-Heat Flux-kW/m^2	Ambient Conditions			
		Temperature °C	Relative Humidity %	Pressure mbar	Cone Set Temperature °C
E2	BFR - 50	24	22	998	731
E4	BFR - 50	22.5	46	974	721
E6	BFR + P - 50	22.5	32	969	721
E8	BFR + P - 50	23	36	980	721
E10	BFR + PHF - 50	23	43	980	721
E30	BFR + PHF- 50	22.5	37	978	725
E12	NFR -100	22.5	45	981	978
E13	NFR -100	24	47	982	978
E15	BFR -100	23	43	975	937
E16	BFR -100	22.5	38	987	927
E18	HFR -100	22.5	44	986	924
E19	HFR -100	22.5	42	986	922
E21	NFR - 50	22.5	38	987	740
E22	NFR - 50	22.5	41	982	736
E24	HFR - 50	23	37	985	736
E25	HFR - 50	23	27	996	736
E27	1556 HFR - 50	22	37	986	727
E28	1556 HFR - 50	22	40	980	725
E32	HFR + P - 50	22	35	995	722
E33	HFR + P - 50	21.5	28	991	722
E35	HFR + PHF - 50	21.5	26	981	721
E36	HFR + PHF - 50	21.5	32	992	721
E38	1556 HFR + P - 50	22	32	981	721
E39	1556 HFR + P - 50	21.5	33	981	721
E41	1556 HFR + PHF - 50	21.5	24	998	719
E42	1556 HFR + PHF - 50	20.5	35	990	719

9 Appendix C: Elemental Analyses of Component Mixtures

Table 9-1. Elemental Analyses of Component Mixtures

Substance	Low Halogen: Total Mass (g) per 3052.25 g of mixture	Non-Low Halogen: Total Mass (g) per 3052.25 g of mixture
1,4-BENZENEDICARBOXYLIC ACID, POLYMER WITH [1,1'-BIPHENYL]-4,4'-DIOL,	845.140	0.000
4-HYDROXYBENZOIC ACID, 6-HYDROXY-2-NAPHTHALENECARBOXYLIC ACID AND N-(4-HYDROXYPHENYL)ACETAMIDE (9CI)	845.140	0.000
1,4-BIS(2,3-EPOXYPROPOXY)BUTANE	0.002	0.002
ACRYLIC RESIN	0.135	0.135
AG (Silver)	8.208	8.208
AL (Aluminum)	0.004	0.004
AL2O3 (Aluminum oxide)	41.150	41.150
ANTIMONY TRIOXIDE	0.000	0.000
ARALDITE GY 250	1.721	1.721
AU (Gold)	7.065	7.065
B (Boron)	0.000	0.000
BARIUM TITANATE(IV)	453.479	453.479
BASIC DUROMER: POLYURETHANE RESIN (COMPOUND OF A POLYMERIC NETWORK)	1.082	1.082
BERYLLIUM	0.000	0.000
BROMINE	0.086	0.085
C.I. PIGMENT BLACK 28	0.281	0.281
CALCIUM	0.000	0.000
CALCIUM MONOXIDE	0.157	0.157
CALCIUM-CARBONATE	1.866	1.866
CARBON BLACK	12.662	1.318
CHLORINE	0.086	5.757
CHROMIUM	0.001	0.001
CHROMIUM(III)OXIDE	0.355	0.355
COBALT, ELEMENTAL	0.615	0.615
COPPER (METALLIC)	425.069	425.069
COPPER OXIDE (CUO)	9.852	9.852
CRISTOBALITE	1.174	1.174
DIIRON-TRIOXIDE	121.742	121.742
DODECANE	0.014	0.014
DUMMY SUBSTANCE	0.002	0.002
Epoxy Resin	33.936	33.936
FE (Iron)	8.160	8.160
FIBROUS-GLASS-WOOL	277.933	453.768
FLOWERS OF ZINC (Zinc Oxide)	29.989	29.989
FORMALDEHYDE, OLIGOMERIC REACTION PRODUCTS WITH 1-CHLORO-2,3-EPOXYPROPANE AND PHENOL	1.906	1.906
FRITS, CHEMICALS	0.280	0.280
FUSED SILICA	374.758	374.758
IN (Indium)	0.000	0.000
LEAD	0.170	0.170
LEAD (II) OXIDE	0.062	0.062
LEAD (II) TITANATE	0.767	0.767
MAGNESIUM TITANIUM OXIDE (MGTIO3)	9.767	9.767
MAGNESIUM-OXIDE	0.131	0.131
MANGANESE	0.031	0.031
MO (Molybdenum)	0.355	0.355
NICKEL	101.263	101.263
NICKEL OXIDE	26.977	26.977
P (Phosphorous)	0.036	0.036
PALLADIUM	0.451	0.451
P-F-R-2	25.913	25.913
Polyphenylene Sulfide		674.980
SI (Silica)	14.265	14.265
SILICA	0.761	0.761
SILICONE	2.555	2.555
SN (Stannum/Tin)	7.623	7.623
SOLVENT NAPHTHA (PETROLEUM), HEAVY AROM.	0.018	0.018
STABILIZATION UV, LIGHT, HEAT	2.094	2.094
TUNGSTEN (W)	0.780	0.780
ZINC POWDER - ZINC DUST (NOT STABILIZED)	199.323	199.323

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