FIRE OF A FLAME RETARDED TV

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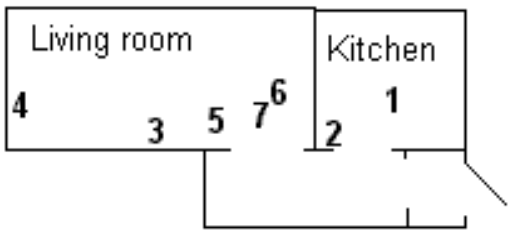
Introduction

In the world of accidental fires there is a growing concern of formation and distribution of toxins and environmentally hazardous compounds. It is well known that brominated flame retardants can form polybrominated dibenso-p-dioxins (PBDD) and polybrominated dibensofurans (PBDF) during fire (1,2). It is also known that the flame retardants themselves can vaporise due to the heat (3). When flame retarded electronics burn, chlorinated material (i.e. chlorinated plastics, plasticerers) are often involved in the combustion. Beside the brominated dioxins and furans, chlorinated and mixed chlorinated, brominated dioxins and furans will then be formed (4). Zelinski et. al. (5,6) has previously investigated accidental fires in flats. These investigations clearly show formation of PCDD, PCDF, PBDD and PBDF in the fires and also findings of brominated flame retardants. During February 1999 we had the opportunity to investigate a flat after a TV and VCR fire. Wipe-test and ash samples were taken for analysis of halogenated dioxins and furans and brominated flame retardants. In these analysis we have focused on tetra chloro-, mixed tetra bromo chloro and tetra bromo dioxins and furans The aim of the study was to investigate how halogenated dioxins and furans are formed from brominated flame retarded material and also to study the behaviour of brominated flame retardant in a fire.

Material and Methods

The fire started in the TV, the process was almost explosively. An eyewitness fled the flat because of smoke formation. Fire fighters extinguished the fire with water before it spread. Affected parts were the TV (Luxor, 1994), VCR, 1-2m^3 wooden floor and 1dm^3 of a sofa. The rest of the flat was unaffected by fire but was all black by a thin layer of soot. Seven samples were sampled; four wipe-tests (soot) and three ashes. The sampling was performed less than two days after the fire, before any cleaning had begun. All wipe-tests were taken on hard surfaces, glass or varnish. All with Kleenex, area 0,3 x 0,3 m^3 and stored in dark glass vials.



Samples:

1. Table, blank sample wipe test under table cloth.
2. Kitchen cupbourd, wipe-test.
3. Book-shelf glas door, wipe-test
4. Window, wipe-test.
5. TV and VCR, ash remainings.
6. Sofa, ash.
7. Pile of ash from TV and wooden floor.

Figure 1. Sketch of flat and sampling points

Ash samples were collected in dark glass vials. Before extraction the ash samples were crushed in mortar. All samples were extracted with toluene in Soxhlet for 12 hours. Before extraction all samples were spiked with 13C PCDD's, PCDF's, 2378tetraBDD, 2378tetraBDF, 1Br2378ClDD and 33'44' tetra bromodiphenyl ether. The extracts were divided into two parts. One part was cleaned-up for dioxin analysis by a silica-gel, H_2SO_4/silica-gel multi-layer column and an alumina oxide (super grade) column. Recovery-spike was added and dioxins analysed on HRGC/HRMS, a VG 250-S with a SP-2330 column and operating with EI. Due to the amount of mixed bromo-chloro dioxin and furan congeners, only some halogenation levels have been investigated. The other extract part was gently cleaned on a silica column deactivated with 10% water. Recovery spike was added and the samples were analysed for brominated flame retardants. A MD-800 HRGC/LRMS operating with EI was used with a DB5 column. Some of the most common brominated flame retardants were used as reference material.

Results and Discussion

Both wipe-test and ash samples contained chloro, chloro-bromo and bromo dioxins and furans (table 1). Most dioxins and furans were found in the living room. Even though the kitchen was as black with soot as the living room, the dioxin and furan levels were less in the kitchen. This can be due to a longer residence time in the living room. As in most combustions with similar fuel, the amount of tetra dioxins is less than of tetra furans. A problem with the comparison of chloro, bromo-chloro and bromo dioxins and furans is the difference in weight, to make a fair comparison of formed amount it is better to make a calculation based on mole. The di bromo di chloro dioxins and furans seems to be favoured compared to tetra chloro or tetra bromo dioxins and furans (either as ng or mole). One reason could be a statistical one, there are more isomer combinations possible for two halogens compared to one halogen. An investigation of which isomers are favoured could give valuable information. The wipe tests were not weighed after sampling, an estimation is that they contained not more than 3 grams of particles. The wipe-tests 3 and 4 then contains more dioxins and furans than the ash samples on gram basis. A difference that can be a parallel to bottom ash and fly ash in an incinerator. The heat close to the flame does not favour formation of dioxins and furans, but above the flame front or in smoke the heat is low enough for formation. The findings of brominated dioxins and furans is an evidence that brominated flame retardants has been used in the combusted materials. The samples contained surprisingly small amounts of brominated flame retarants (table 2), considering the dioxin and furan formation. There are many possible explanations, for instance;

-A less common flame retardant has been used in the TV and VCR.
-Evaporated flame retardant molecules has received energy enough to rearrange.
-Most of the flame retardant has been consumed in the fire and formed more stable molecules like dioxins and furans or HBr and Br_2

These analysis confirms earlier investigations showing that large amounts of brominated and mixed bromo-chloro dioxins and furans can be formed in accidental fires where brominated flame retardants are used. The total amount of 2378 TeBDF formed from the TV and VCR can roughly be estimated. The living room total area is about $100m^2$ (floor, ceiling and walls), and based on sample 4 the total amount in soot is approximately 220ng 2378-teBDF and 0,4mg total teXDF. The amount of ash formed can only roughly be estimated to 1-2 kilos, the ash contribution is then 0,2-0,4mg total teXDF in ash. Altogether 0,6-0,8mg teXDF from the fire.

Unit	ng/m^3 (p mole/m^3)				ng/g (p mole/g)		
Sample	1	2	3	4	5	6	7
2378 tetra Cl DF	nd	0.1	1.5	4.7	0.01	0.1	0.02
Σ tetra Cl DF	nd	1.8 (5.8)	121 (397)	301 (987)	0.5 (1.6)	3.3 (11)	1.0 (3.2)
2377 tetra Cl DD	nd	0.1	0.1	0.1	nd	0.01	0.004
Σ tetra Cl DD	0.5 (1.5)	0.8 (2.5)	3.1 (9.7)	13 (40)	nd	0.3 (1.1)	0.2 (0.73)
3Br 278 Cl DF	nd	0.2	0.3	1.3	0.01	0.002	0.02
Σ moBr triCl DF	2.1 (6.0)	4.8 (14)	329 (939)	913 (2600)	1.4 (3.9)	1.0 (2.9)	4.0 (11)
2 Br 378 Cl DD	nd	nd	nd	nd	nd	nd	nd
Σ moBr triCl DD	1.7 (4.7)	1.2 (3.2)	0.9 (2.6)	4.9 (13)	nd (nd)	nd (nd)	0.9 (2.5)
Σ di Br di Cl DF	59 (167)	57 (163)	959 (2733)	2456 (6998)	8.4 (24)	3.8 (11)	18 (53)
23 di Br 78 di Cl DD	nd	nd	0.3	1.7	nd	nd	nd
Σ di Br di Cl DD	2.3 (6.3)	nd	32 (87)	91 (249)	0.1 (0.25)	0.4 (1.1)	0.3 (0.71)
2378 tetra Br DF	nd	nd	3.2	2.2	nd	0.01	0.3
Σ tetra Br DF	nd	63 (130)	928 (1922)	1157 (2395)	24 (50)	4.3 (9.0)	177 (366)
2378 tetra Br DD	nd	nd	nd	nd	nd	nd	nd
Σ tetra Br DD	nd	nd	nd	33 (67)	nd	nd	nd

Table 1. Levels of tetrahalogenated dioxins and furans in wipe test and ash samples.

Unit	ng/dm^3				ng/g		
Sample	1	2	3	4	5	6	7
TBBP-A	nd	nd	nd	nd	nd	nd	nd
TeBDE	nd	nd	nd	190	nd	10	4
PeBDE	nd	nd	nd	nd	nd	9	3
HxBB	na	na	nd	na	na	na	na
TBBP-A (Tetrabromobisphenol A), TeBDE (Tetrabromobiphenylether), PeBDE (Pentabromobiphenylether), HxBB (Hexabromobiphenyl),							

Table 2. Levels of some common brominated flame retardants in wipe test and ash samples.
nd - not detected , na - not analysed

Brominated dioxins and furans seems to be in the same toxic range as chlorinated (7). The wipe test in these analysis corresponds to what is spread with smoke. Inhaled smoke can, beside acute-toxic gases, perform an exposure of long-term toxicity compounds. The exposure is a potential risk for people getting in direct contact with the smoke, soot and ash formed after a fire with brominated flame retardant involved. The use of brominated flame retardant thus demands a thorough cleaning after a fire.

Acknowledgements
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