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PROCESSING WASTES AND WASTE-DERIVED FUELS CONTAINING BROMINATED FLAME RETARDANTS

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Preface

Brominated flame retardants (BFRs) are widely used, often together with antimony-based flame retardants, in electronic and electric equipment, furniture and office equipment. While this increases the fire safety for these products, the BFRs are problematic when thermal processes are used during the treatment of waste streams from these products, such as waste from electrical and electronic equipment (WEEE). Not only do the BFRs negatively effect the incineration of old furniture, they interfere with thermal processes that aim at the recovery of, for example, valuable metals from WEEE.

This report gives an overview of which and how much BFRs are found in various products and waste streams and what problems this may bring to thermal processes for recovery and recycling or during incineration or waste-to-energy processing. Also the formation of brominated analogues of dioxins and furans, PBDD/Fs (poly brominated dibenzo -p- dioxins and - furans) is addressed, and analytical methods that allow for the identification and measurement of concentrations of brominated chemicals during thermal processing of BFR-containing waste streams.

What is *not* given in this report is a discussion on different waste treatment methods and how all these are affected by BFRs. Also, the issue of bromine-related corrosion is mentioned but could not be analysed in depth due to a lack of relevant literature. The same holds for the consequences of methyl bromide (or bromoform, CH_3Br) being an ozone depleting substance. Instead, this study aimed at summarising the reasons for, and consequences of the presence of BFR compounds in waste streams, while taking into consideration the options for recovery of bromine.

This study was funded by Ekokem Oy Ab support funding (*apurahoitus*) 2001.

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List of Abbreviations

1. Introduction

Brominated flame retardants (BFRs) are widely used, often together with antimony-based flame retardants, in electronic and electric equipment, furniture and office equipment. While this increases the fire safety for these products, the BFRs are problematic when thermal processes are used during the treatment of waste streams from these products, such as waste from electrical and electronic equipment (WEEE). Not only do the BFRs negatively effect the incineration of old furniture, they interfere with thermal processes that aim at the recovery of, for example, valuable metals from WEEE.

A flame retardant should inhibit or suppress a combustion process and that's why they are used in products which would otherwise have a high risk of fire. Including flame retardant into products is one way to improve their fire safety relatively cheap way. Depending on their nature, flame retardants can act chemically and/or physically in solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, *e.g.* during heating, decomposition, ignition or flame spread [1]. For BFRs the high molecular weight provides numerous advantages from manufacturers point of view are such as low volatility, low migration rates at surface, ease of handling.

This report gives an overview of which and how much BFRs are found in various products and waste streams and what problems this may bring to thermal processes for recovery and recycling or during incineration or waste-to-energy processing. Also the formation of brominated analogues of dioxins and furans, PBDD/Fs (poly brominated dibenzo -p- dioxins and - furans) is addressed, and analytical methods that allow for the identification and measurement of concentrations of brominated chemicals during thermal processing of BFR-containing waste streams.

Bromine-related corrosion and the ozone depleting properties of methyl bromide (bromoform) are mentioned but not discussed.

2. The Chemistry of Brominated Flame Retards

2.1 *Types of flame retardants*

Flame retardants are added to polymeric materials, both natural and synthetic, to enhance the flame-retardancy properties of the polymers.

There are four main groups of flame retardant chemicals:

- Inorganic flame retardants including aluminium trioxide, magnesium hydroxide, ammonium polyphosphate and red phosphorous.
- Halogenated flame retardants, primarily based on chlorine and bromine. The brominated flame retardants are included in this group.
- Organophosphorous flame retardants are primarily phosphate esters. Organophosphorous flame retardants may contain bromine or chloride.
- Nitrogen-based organic flame retardants are used for a limited number of polymers.

2.2 *Mechanisms of action*

Depending on their type, flame retardants can act chemically and/or physically in the solid, liquid or gas phase. They interfere with combustion during a particular stage of this process, *e.g.* during heating, decomposition, ignition or flame spread. Substitution of one type of flame retardants by another means a change in the mechanisms of flame retardancy.

Halogen containing flame retardants act primarily by a chemical interference with the radical chain mechanism taking place in the gas phase during combustion. High-energy OH and H radicals formed during combustion are removed by bromine released from the flame retardant as described in reactions 1-7. The basic concept is given in Figure 1.



The halogen retardant RX initially breaks down:



where X is either Cl or Br. The halogen radical reacts to form the hydrogen halide as described in reaction 4:



which in turn interferes with the radical chain mechanism shown in reactions 5 and 6:



The high energy H and OH radicals are removed by reactions with HX and replaced with low energy X radicals. The actual retardant effect is thus produced by HX. The hydrogen halide consumed is regenerated by reaction with hydrocarbon as in reaction 7:



Thus HX ultimately acts as a (negative) catalyst. The radical interception mechanism is questioned by E.R. Larsen (for example in *Fire & Flammability* 10, 1979) who surmises that physical mechanism lies behind the flame retardant effect of halogen compounds. After all, hydrogen halides are non-flammable gases but also form non-combustible protective layers interfering with or halting the combustion process. [1]

Several authors have pointed out that halogen containing flame retardants are also effective in the condensed phase. [1]

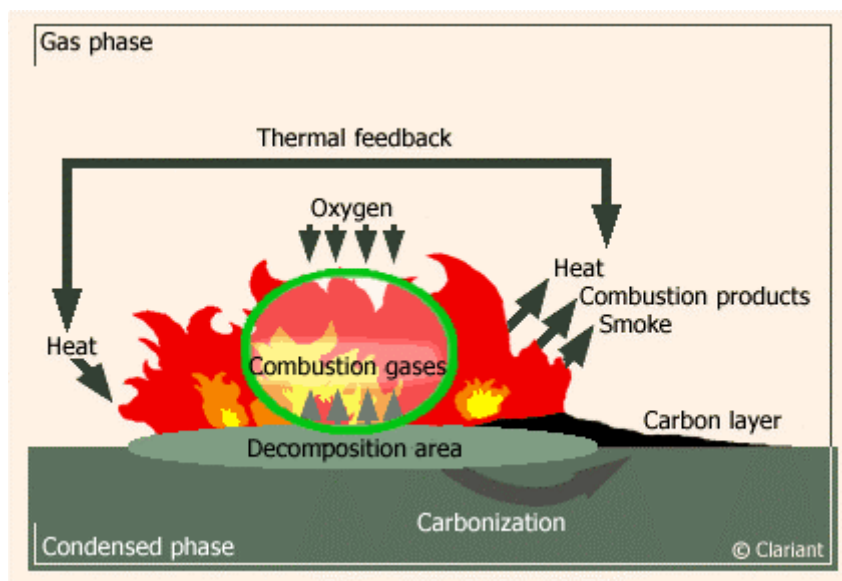


Figure 1 BFR acting principles: interruption of the radical chain mechanism of the combustion process in the gas phase. (picture taken from [2])

Although brominated flame retardants are a highly diverse group of compounds the flame-retardancy mechanism is basically the same for all compounds. However, there are differences in flame-retardancy performance of the brominated compounds, as the presence of these compounds in a polymer will influence the physical properties of the polymer.

In general aliphatic bromine compounds are easier to break down and hence more effective at lower temperatures, but also less temperature resistant than aromatic retardants. [1]

Aluminium hydroxide and other hydroxides act in a combination of various processes. When heated the hydroxides release water vapour that cool the substrate to a temperature below that required for sustaining of the combustion processes. The water vapour liberated has also a diluting effect on the gas phase and forms an oxygen-displacing protective layer. Additionally the oxide (*e.g.* AlO_2) forms, together with the charring products, an insulating protective layer.

Phosphorous compounds mainly influence the reactions taking place in the solid phase. By thermal decomposition the flame retardant is converted to phosphorous acid, which extracts water from the pyrolysing substrate, causing it to char. However, some phosphorous compounds may, similar to halogens, act in the gas phase as well by a radical trap mechanism.

Nitrogen-based flame retardants like melamine and melamine derivatives act by intumescence. These flame retardants are most often used in combination with other flame retardants. Gases released from the compounds make the material swell and form a insulating char on the surface.

A distinction is made between reactive and additive flame retardants. Reactive flame retardants are built chemically into the polymer molecule, together with the other starting components. This prevents them from bleeding out of the polymer and vaporise and their flame retardancy is thus retained. They have no plasticising effect and do not affect the thermal stability of the polymer. They are used mainly in thermosets, especially polyesters, epoxy resins and polyurethanes (PUR) in which they can be easily incorporated.

The most widely used reactive brominated flame retardants are tetrabromobisphenol A (TBBPA), tetrabromophthalic anhydride, dibromoneopentylglycol, and brominated styrene.

Additive flame retardants are incorporated in the plastic either prior to, during, or, more frequently, following polymerisation. They are used especially in thermoplastics such as ABS, HIPS, PS, PC and thermoplastic polyesters. If they are compatible with the plastic they act as plasticisers, otherwise they are considered to be fillers. They are sometimes volatile and tend to bleed, so their flame retardancy may be gradually lost. High molecular weight products are developed to enable plastics to be made more permanently fire retardant by the additive method.

The most used additive brominated flame retardants are polybrominated diphenyl ethers (PBDEs), tetrabromobisphenol A (mostly used as reactive FR) and hexabromocyclododecane (HBCD).

2.3 Synergism, antimony oxide

Combinations of flame retardants can produce an additive or a synergistic effect. While the additive effect is the sum of the individual actions, the effects of synergism are higher than this sum.

Antimony trioxide, Sb_2O_3 , the main antimony compound used commercially, shows no perceptible flame-retardant action on its own. Together with bromine-containing compounds, however, it produces a marked synergistic effect. Antimony trioxide is widely used in brominated FR formulations.

2.4 Chemical properties of bromine

Bromine has two stable isotopes (mass number 79 and 81) present in the earth's surface layer for 50.5% as ^{79}Br and 49.5% as ^{81}Br . There are 35 electrons in the electron shells, 35 protons in the nucleus, and 44 and 46 neutrons, respectively in the nuclei of the two stable isotopes. Both isotopes have nuclear spins of 3/2 and exhibit quadrupole moments. The electronic configuration in the valence shell is $4s^2 4p^2$, lacking one from having the inert gas configuration. Bromine has a strong affinity for a complete the outer shell, but somewhat weaker than for chlorine. This is because the nuclear attraction for the valence electrons is more screened in bromine than in chlorine. The effect of this may be seen from the values for ionization potentials, and the dissociation constant of Br_2 and Cl_2 at a given temperature. [3]

Bromine adds to double and triple bonds and it participates similar to chlorine in substitution reactions. The principal differences to chlorine are attributed to the larger size of the bromine atom with its larger number of electrons screening the attraction of the nucleus on valence shell electrons. Thus, despite the oxidising power of bromine the formation of some fully brominated structures is difficult. [3]

3. The Properties of Brominated Flame Retardants

A BFR may be defined as “a non-organo phosphorus organic compound where one or more hydrogen atoms are replaced by bromine” [4]. This definition excludes ammonium bromide and brominated organophosphates. BFRs contain 50-95 %-wt bromine, and can be separated into aromatic, aliphatic and cyclo-aliphatic. There are over 40 different BFR types in commercial use but basically only a handful of those are used on a large scale.

The aromatic BFRs can be divided into three types, *i.e.* polybrominated diphenyl ethers (PBDEs), tetrabromo bisphenol A (TBBPA) and its derivatives, and polybrominated biphenyls (PBBs). Of the cycloaliphatic BFRs compounds, hexabromocyclododecane (HBCD) is the most important. Aliphatic BFRs are not used in large amounts since they are less stable than aromatic BFRs; they may be more effective at lower temperatures, however. Each of these BFRs has very different properties and that why it's important to know which kind of BFR is discussed. Different types of BFRs should never be assimilated when referred to, especially when it comes to toxicological issues.

3.1 Tetrabromobisphenol A

The most widely used BFR compound nowadays is tetrabromobisphenol A, TBBPA. Its trade name is FR-1524. TBBPAs and their derivatives such as TBBPA bis-(2-hydroxyethylether) are a group of aromatic BFRs in which four hydrogens in the bisphenol structure are replaced by bromine (see Figure 2). Their market share is currently over 50% world wide.

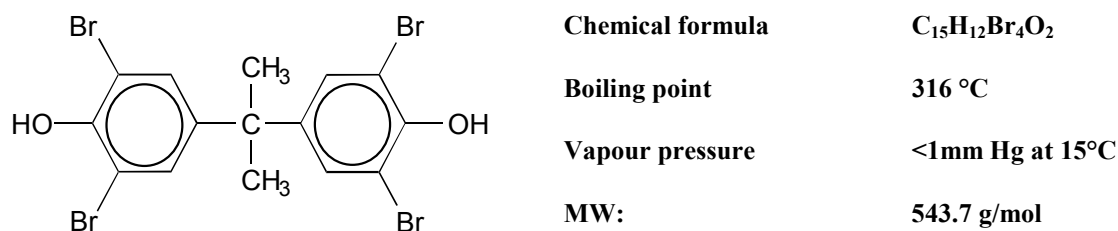


Figure 2. Tetrabromobisphenol A (TBBPA). (picture taken from [4])

TBBPA's and derivatives' main use were as reactive FR for unsaturated polyester (UPE) and as additive FR for polybutylene terephthalate (PBT), polyethylene terephthalate (PET) and ABS plastics [4]. Some of the major applications for TBBPA have been in printed circuit board laminates, housings of electric or electronic equipment such as PC monitors and in transportation applications such as a car's plastic parts.

Typical properties of TBBPA are listed in Table 1.

Table 1 Properties of TBBPA. [5]

Appearance	White crystalline powder
Bromine content %	58.5
Specific gravity g/cc	2.17
Assay [HPLC] %	99
Melting point °C	181
Moisture %-wt	0.1
Color APHA in methanol 20%	10
Bromides ppm	75

Results from a thermogravimetric analysis (heat up 10 °C/minute, in air), are presented in Table 2.

Table 2. Thermogravimetric analysis on TBBPA. [5]

Weight loss %	Temperature °C
2	285
5	305
10	315

3.2 Polybrominated diphenyl ethers (PBDEs)

Polybrominated diphenyl ethers are the most interesting and the most discussed BFRs because of their wide use in electric and electronic appliances. PBDEs are a group of aromatic brominated compounds in which one to ten hydrogens in a diphenyl oxide structure are replaced by bromine. PBDEs have a large number of congeners, depending on the number or position of bromine atoms on the two phenyl rings. The total number of possible congeners is 209, and numbers of isomers for mono-, di-, tri-, up to decabromo diphenyl ethers are: 3, 12, 24, 42, 26, 42, 24, 12, 3 and 1. Technical PDBE products are produced by brominating diphenyl ether in the presence of a catalyst. [6]

PBDEs can be divided into two different groups according their bromine content: lower such as Tetra-BDE, Penta-BDE and Hexa-BDE or a higher content such as Hepta-, Nona-BDE, Deca-BDE and Octa-BDE, of which Deca-BDE (see Figure 3) is according to the Bromine Science and Environmental Forum the most common compound (see Table 14). According to laboratory experiments made by Watanabe and Tatsukawa in 1987, Deca-BDE has been shown to photolytically degrade and form lower brominated PBDE. [6]

Major uses for PBDEs are plastic housings of smaller office equipment *etc.* (which are usually made of high impact polystyrene HIPS plastic) and in PE plastics. Nowadays PBDEs' market share is declining while manufacturers are switching their flame retardants to non-halogen ones. The main reason for this trend has been environmental concern about PBDEs toxicological effects [6] and (up)coming regulation changes especially in Europe [7].

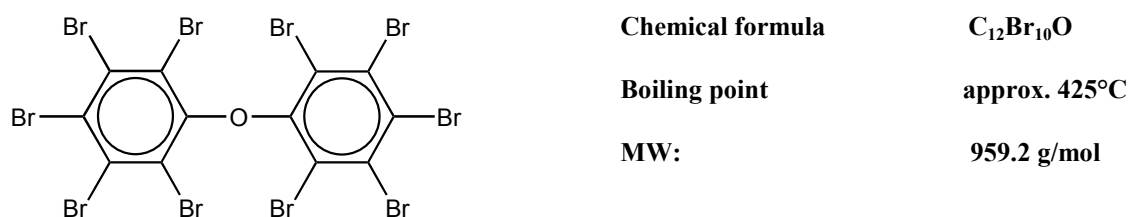


Figure 3. FR-1210 Decabromodiphenyl ether (DeBDE). (picture taken from [4])

Typical properties of DeBDE are listed in Table 3.

Table 3. Properties of De-BDE. [5]

Appearance	Free flowing micronized, white to off-white powder
Bromine content %	83
Specific gravity	3
Assay (HPLC) %	97
Melting range °C	303-307

Results from a thermogravimetric analysis of De-BDE (heat-up 10 °C/minute, in air), are presented in Table 4.

Table 4. Thermogravimetric analysis on DeBDE. [4,5]

Weight loss %	Temperature °C
1	319.5-322
5	353.10-362
10	370.5-385
50	414
90	436

Printed circuit boards typically do not contain any of the three commercial PBDEs. [8] In the literature it is mentioned that Asian types of phenolic paper/laminate could contain PBDE. [9]

The commercial PBDE are produced by the bromination of diphenyl oxide under certain conditions, which results in products containing mixtures of brominated diphenyl ethers. The commercial PBDEs are rather stable compounds with boiling points ranging between 310 and 425 °C and low vapour pressures, *e.g.*, 3.85-13.3 Pa at 20-25 °C; they are lipophilic substances. Their solubility to water is very poor, especially that of the higher brominated diphenyl ethers, and the n-octanol/water partition coefficients range between 4.28 and 9.9. Polybrominated diphenyl ethers have not been reported to occur naturally in the environment, but other types of BDE have been found in marine organisms. [6]

Table 5 presents compositions of commercial brominated diphenyl ethers.

Table 5. Composition of commercial brominated diphenyl ethers. [6]

Product	Composition					
	PBDE	TrBDE	TeBDE	PeBDE	HxBDE	HpBDE
DeBDE						
OcBDE					10-12%	42-44%
PEBDE		0-1%	24-38%	50-62%	4-8%	
TeBDE	7.6%	--	41-41.7%	44.4-45%	6-7%	

3.3 Polybrominated biphenyls (PBBs)

Polybrominated biphenyls (PBBs) are a group of halogenated hydrocarbons which are formed by substituting bromine for hydrogen in biphenyl (see Figure 4). According to the OECD, decabromobiphenyl (DeBB) is the only brominated biphenyl that has been identified in commercial use. DeBB has traditionally been used as additive flame retardant for styrenic polymers and engineering plastics [4]. PBBs can be found in TV and computer housings and textiles.

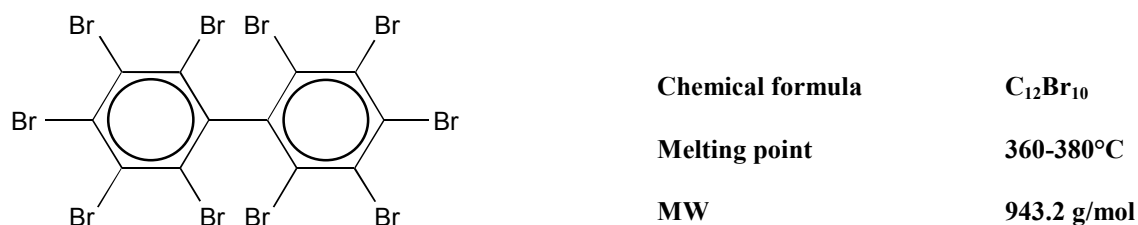
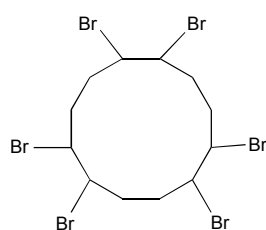


Figure 4. Decabromobiphenyl (DeBB). (picture taken from [4])

Nowadays the production of PBBs has been phased out [8] but it'll take years before all PBB-containing items have reached the end of their life cycle and waste management doesn't have to consider of these compounds anymore.

3.4 Hexabromocyclododecane (HBCD)

Hexabromocyclododecane (HBCD) is a cycloaliphatic compound with six bromine atoms (see Figure 5). HBCD is produced by bromination of cyclododecane in a batch process. HBCD has been used for about 20 years [10]. Major users of HBCD are textile industry (coatings) and building and construction industry (flame retarded insulation). End products containing HBCD include upholstered furniture, building materials and interior textiles and cushions for vehicles.



Chemical formula	C₁₂H₁₈Br₆
Decomposition point	> 200°C
Vapour pressure	<133 Pa at 20°C
MW	641.4 g/mol

Figure 5. Hexabromocyclododecane (HBCD). (picture taken from [4])

3.5 Other BFRs

The above mentioned brominated flame retardants represented about 76% of the 1992 global production of BFRs. [4] The remaining is covered by a number of other retardants. The most of them are presented briefly in Table 6.

Table 6 Other BFRs and their use. [4]

Chemical	Bromine content (%)	Reactive	Additive	Main applications (globally)
TBPA diester/ether diol	45	+		rigid PUR foams
Ethylene bis(tetrabromophthalimide) (EBTBP)	67		+	similar to DeBDE
Tetrabromophthalimide	69		+	engin. thermoplast.
Disodium salt of tetrabromophthalate	15		+	textile, coatings
Dibromoethyldibromocyclohexane	75		+	PS, PUR
Ethylene bis(dibromonorbornanedicarboximide)	48		+	nylons and polyolefins
Dibromoneopentyl glycol (DBNPG)	61	+		UPE, PUR
Tribromoneopentyl alcohol (TBNPA)	72	+		PUR
Vinyl bromide (VBr)	75	+		modacrylic fibers
2,4,6-Tribromophenol (TBP)	73	+		phenolics, epoxy
Bis(tribromophenoxy)ethane (HBPE)	70		+	ABS, PC, thermosets
Poly(dibromophenylene oxide) (PDBPO)	62		+	similar to DeBDE
Pentabromoethylbenzene (5BEB)	82		+	UPE, SBR, textile
Poly(pentabromobenzyl acrylate) (PBB-PA)	70		+	polymeric, PBT
Polydibromostyrene (PDBS)	59		+	PA, PBT, styrenics
Brominated polystyrene (BrPS)	60		+	PBT, PS

4. BFRs in Consumer Products and E+E Equipment

4.1 BFRs in Textiles

Brominated flame retardants can be found in the following textiles: upholstered furniture, clothing, particularly protective clothing, carpets, curtains, tents, vehicle interiors (excluding airplanes), offices, public and larger premises, glass fibre products and other technical textiles. [4]

Flames from cigarettes, candles or matches are typical reason for residential fire deaths. Flame retard chemicals can be incorporated within fibres, applied to the surface of the textile, or applied to the back of the textile in the form of a polymeric coating. [11] It is estimated that FR chemicals would be applied as formulations in as much as 600 square yards of upholstery fabrics each year. [12]

Flame retardants must have an element of transferability from the back into the whole fabric and therefore they are almost always based on so-called vapor-phase active antimony-bromine (or other halogen). Products comprise brominated species such as DeBPE or HBCD and Sb_2O_3 . [12]

Antimony-halogen flame retardants are currently the most successful within the back-coated textile areas when considering cost and effectiveness. Unlike the fibre reactive, durable phosphorous- and nitrogen - containing flame retardants used in cellulosic fibres, they can only be applied topically in a resin binder, usually as a back-coating. [12]

"The worst case scenario" numbers for total add-on of FR agent in fabrics are 25% for both Sb-DBDPE and Sb-HBCD where the mass fraction for Br is 12% and for Sb 7% in both cases. [12]

Table 7 lists durably-finished and inherent flame retardand fibres in common use.

Table 7. Durably-finished and inherent flame retardant fibres in common use [12]

Fibre	Flame Retardant Structural Components	Mode of Introduction*
<i>Natural</i>		
Cotton	Organo-phosphorous and nitrogen-containing monomeric or reactive species	F
Wool	Antimony-organo-halogen systems	F
<i>Regenerated</i>		
Viscose	Organo-phosphorous and nitrogen/sulphur containing species, polysilicic acid and complexes	A
<i>Inherent Synthetic</i>		
Polyester	Organo-phosphorous species: Phosphinic acidic comonomer, phosphorous containing additive	C
Acrylic	Halogenated comonomer (35-50% w/w) plus antimony compounds	C
Polypropylene	Halo-organic compounds usually as brominated derivatives	A
Polyhaloalkenes	PVC, polyvinylidene chloride	H
<i>High heat and flame resistant (aromatic)</i>		
Polyaramids	Poly(m-phenylene isophthalamide), poly(p-phenylene terephthalamide)	Ar

* F = Chemical finish ; A = Additive introduced during fiber production; C = Copolymeric modifications; H = Homopolymer; Ar = Aromatic homo- or copolymer

The expanded polystyrene stuffing in sack chairs, health mattresses, nursing cushions, *etc.*, is normally flame retarded with between 0.5% and 1% HBCD. [12] Worldwide, tents are one of the major textile end-products for BFRs. They are used both military tents and civil tents, especially "party" tents. [12] The used BFRs are most likely the same decabromo-diphenyl oxide or hexabromocyclododecane and Sb_2O_3 as in the back-coated textile areas.

Industry information indicates that PBDEs or other BFRs might be present in flame retarded carpets based on cheaper synthetic fibres, where they are encapsulated within the polymer fibres. [12]

Many large manufacturers have voluntarily chosen to abstain from the use of BFRs in their furniture and textile range. For example IKEA’s policy is to use flame retardants only when legislation makes this necessary and in those cases choose alternatives for BFRs.

4.2 BFRs in E+E equipment

Electric and electronic (E+E) equipment usually accounts for the best known and well-studied consumption of BFRs. Typical targets of interest are printed circuit boards and housing of electric and electronic products. Other sources for E+E BFRs are lighting, wirings and housings of electronic appliances. A reason for this special interest can be noticed from Figure 6 where a compilation of statistics on reasons for residential fires in Finland have been presented.

Residential fires in apartment house

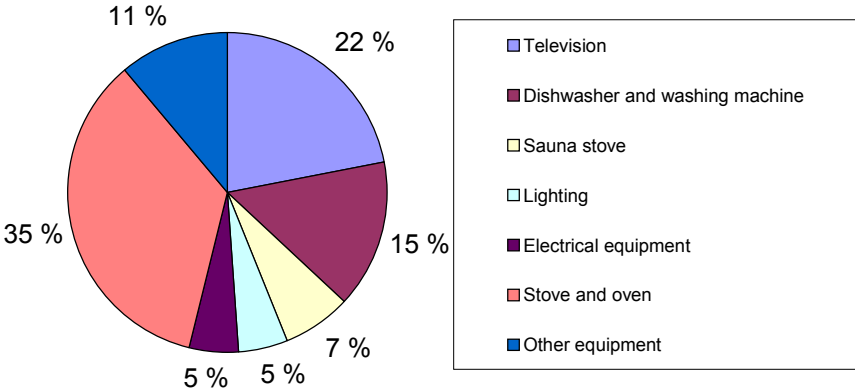


Figure 6 A source of inflammation in residential fires in apartment houses in Finland. [13]

4.2.1 Printed Circuit Boards

Printed circuit boards are assemblies consisting of a copper-foiled laminate over a glass fibre "heart" on which small electric and electronic components, encapsulated in plastic (more common) and metal, are mounted. Both the laminates and the plastic for encapsulation are flame retarded, usually with brominated flame retardans. [4]

There are 2 main groups of laminates, being flexible and non-flexible ones.

The reinforced non-flexible laminates consist usually of either glass fibre reinforced epoxy (FR 4), or cellulose paper reinforced phenolic resin (FR 2). FR4 is the most used laminate nowadays and it usually contains 15% TBBPA. In industrial and office electronics, *e.g.* computers and electronics for telecommunication, the circuit boards are generally based on FR4 or similar type of laminate. The TBBPA content of the most used 1.6 mm FR4 laminate can be estimated at 0.42 kg/m². [4]

By the early 1990s FR2 laminates were flame retarded with TBBPA in Europe and with PeBDE in Asia. For both types the content of a typical FR2 laminate has been estimated at 0.036 kg/m². During recent years it seems there has been a shift away from PeBDE, and today most Asian FR2 laminates seem to be retarded with TBBPA. As a rough estimate it is assumed that PBDEs still cover 30% of the FR2 laminates in consumer electronics other than TV-sets. [4]

Traditionally printed circuit boards for TV sets and home electronic appliances have been based on FR2, but within high-priced market segments there has been a trend towards circuit boards based on FR4. It can however be assumed that FR2 is still the dominating laminate in this area of E+E equipment.

Plastic encapsulation of electronic components on a circuit board is predominantly made of epoxy resin with TBBPA. Of the top ten component groups by volume, seven groups contain TBBPA. These groups are plastic/paper capacitors, microprocessors, bipolar power transistors, IGBT power modules, ASICs, and metal oxide varistors. None of the top ten groups contain other brominated flame retardants. [4]

The concentration of TBBPA in the plastic encapsulations is relatively low. The plastic encapsulation of an integrated circuit (chip) is reported to contain approx. 20-30% epoxy with approx. 2% TBBPA incorporated.

Various analyses of printed circuit board waste from the literature are presented in Table 8.

Table 8. Several analyses of printed circuit board waste.

	Taiwan, 1999 [14]	Europe, 2001 [15]	Europe, 2000 [16]	German report 1992 [17]
Carbon	52.21	42.5	53.7	19
Hydrogen	6.11	5.03	5.59	
Oxygen	Balance	22.01		
Nitrogen	2.56	3.72		
Bromine	8.53	4.97	1.85	4
Sulfur	Trace	0.032	0.08	
Chlorine	Trace	0.023	2.3	
Copper	9.53	4.21		7
Moisture	3.50	1.7		

4.2.2 Housing of Electric and Electronic Equipment

There are two basic reasons why TV- sets are one of the major sources of domestical fires. TVs and monitors are usually quite hot because a cathode ray tube needs certain working temperature and they are usually collecting significant amounts of dust through the ventilation holes. This is the reason why housings of computer monitors and TV sets are major applications for BFRs, mainly PDBEs. In the United States, Canada, Australia and Japan there has been very strict legislation in order to make monitors and TVs more safe and in year 2002 new EU standards will be set for fire safety of TV sets. However, it won't probably increase the consumption of BFRs because the industry has moved towards bromine-free flame retardants.

Housings or enclosures for computer monitors and other appliances are predominantly made from high-impact polystyrene (HIPS), ABS-polycarbonate blends or ABS-based flame retardant compounds, although polypropylene (PP), polycarbonate (PC) and blends of polyphenylene ether (PPE) and styrene/butadiene polymer may be used as well. In the early 1990s, HIPS represented 30% of the global De-BDE consumption, and ABS accounted for around 95% of the total Oc-BDE supplied in the EU. [4]

Back panels - and to some extent the front cabinet - of TV sets are usually made of flame retarded materials. In the USA and Japan, BFRs are still used in back panels and the front cabinet (USA) of TV sets, but in TV sets purchased in Europe the front cabinet does not contain flame retardants, and there is a trend away from the use of halogenated additives in back panels. Based on the monitoring of the German magazine *Stiftung Warentest* it has been shown that the percentage of tested TV set enclosures that contained halogenated flame

retardants decreased from 68% in 1994 to 8% in 1997 as shown in Figure 7. It should be noted that the different tests do not cover the same market segment; some of the test for example only include 17" TV sets. However, the trend seems to be clear. The absence of BFRs in European TV sets and the possible effect on the flammability of the TV sets have been discussed in media. [4]

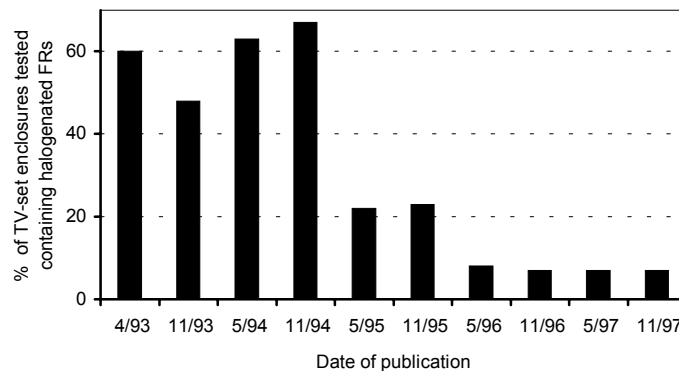


Figure 7. Percentage of tested TV set enclosures containing halogenated flame retardants according to several journal articles. (picture taken from [4])

In year 2000 Finland's Safety Technology Authority (TUKES) has tested twenty-one TVs and one PC monitor type in flammability tests. They analysed for inorganic elements and compounds with SEM+EDS analysers and with XRD, respectively. The results are presented in Table 9.

On the basis of Table 9, probably only one Italian-made Phillips TV set has bromine-based FR included in its housing. There are still many unidentified spectral peaks but non of them are related to bromine compounds, because there isn't any elemental bromine found.

The most of other consumer electronics - radios, videos, *etc.* - are considered not to contain BFRs in the housing. [4] The housing of office machines - computers, printers, copying machines, fax machines, *etc.* - is made of flame retarded plastic. PBDEs have traditionally been used for flame retardancy, but during the last years TBBPA and non-halogen flame retardants have been substituted for the PBDEs.

Table 9. Flammability tests with various TV sets made in Finland 2000. [18]

Type	Country of manufacture	inorganic elements (SEM+EDS)	inorganic compounds (XRD)
Finlux 502 21 C sport	Finland	-	-
Schneider Euro 245 Nicam	Germany	calcium, barium, sulphate	baryta white (barium sulphate) BaSO ₄
Schneider Scenaro 215 SN	Germany	calcium	not indentified
Nokia SP 55 B1	Germany	calcium	calcium carbonate CaCO ₃
Salora MP 2 55 A2	UK	calcium	calcium carbonate CaCO ₃
Salora 28 M 91 Nicam/PIP	Finland	-	-
Finlux 5028 (u) 28 U 40 TX	Finland	-	-
Sharp 70CS-03SN	Spain	phosphorous	(phosphor compound, not identified)
Sanyo 28ER15N EB4-A28	UK	-	-
Philips PZ1 20PT1553/11	Europe	magnesium, silicon, aluminum, calcium, titanium	aluminium oxide borate Al ₅ (BO ₃)O ₆ , cyanate, (magnesiumsilicate)
Philips 20PT155B/13 S	Italy	antimony, bromine	antimony oxide Sb ₂ O ₃ , (bromine compound, not identified)
Sony KV C2983E	Spain	antimony, phosphorous	antimony oxide Sb ₂ O ₃ , (phosphorous compound, not identified)
Salora MP 51 A2	Germany	barium, sulphurous	barium sulphate BaSO ₄
Oceanic 7294 Cinescreen	Finland	magnesium, alumium, silicon	not identified peaks
Philips 28PT4323/11	France	-	-
Sony KV 29X 5E	Spain	antimony, titanium, chrome, phosphorous	
Nokia 6355 Nicam ID	Germany	barium, sulphur	barium sulphate BaSO ₄
Sony KV-25X1E	UK	antimony, titanium, chrome, phosphorous	
Sony KV-25X5E	Spain	antimony, titanium, chrome, phosphorous	not identified peaks
Philips 28PT4473/11 SL6.2	France	calcium, titanium	not identified peaks
Philips 28PT4323/11 SL6.2	France	-	-
Compaq model n:o PE1110T 17".		magnesium, titanium, silicon, phosphorous	magnesium hydroxide Mg(OH) ₂ , melamine phosphate

Test results of electronic products on the German market show that out of more than 150 computer monitors, notebooks (portable computers) and printers tested in 1997/98, none contained PBDEs or PBBs (the source of information is confidential). Of the bromine containing products 72% contained TBBPA. The remaining 28% contained other non-identified BFRs. [4]

4.3 Building materials

There are basically three different applications for potential BFR source in building materials: synthetic insulation materials, translucent and glass fibre reinforced panels and polyolefin based foils. In insulation materials expanded polystyrene (EPS), extruded polystyrene foams (XPS) and polyurethane foams (PUR foams) can contain BFRs.

EPS and XPS are at large used for comparable purposes. Still, XPS is more durable and more expensive than EPS, and this does influence the actual application of the two materials. In Europe, both materials are normally flame retarded with hexabromocyclododecane (HBCD). In EPS between 0.5 wt-% and 1 wt-% is found, and in XPS between 1 wt-% and 2 wt-% is found. [4]

PUR may be flame retarded with both additive and reactive brominated flame retardants. The dominant flame retardants for polyurethanes are brominated polyols, which are reactive flame retardants. If requirements are strict, other additives and reactives may be combined with the brominated polyol. In a number of applications flame retardants, and hence also BFRs, are not used. These are home-refrigerators and district heating pipes (some indoor uses *e.g.* in factories may imply the use of BFRs).

4.4 Other applications of BFRs : paint, transportation

Paints can be flame retarded for fire protection of steel and wood constructions. Other types are "Low flame spread" paints that have no protective effect, but are included also as not to nourish and spread a fire. Table 10 lists the amounts and types of BFRs which are used in paints, fillers and fire proofing panels in Denmark.

Table 10. Consumption of brominated flame retardants with paint, wood impregnation and fillers in Denmark 1997. [4]

Product group	Total consumption of BFRs		Consumption of specific compounds (tonnes)				
	Tonnes	Trend	PBDE	TBBPA	PBB	HBCD	Other BFRs
Paint	0.1-0.3	?	0.1-0.3				
Fire proofing for wood	0.5-1.2	?					0.5-1.2
Joint fillers etc.	<0.2	?	<0.2				
Total (round)	0.6-1.7		0.1-0.5				0.5-1.2

Basically, industry uses non-brominated compounds in applications such described in Table 10. These FR types include nitrogen and phosphorous flame retardants. Exception is PUR based fillers which were presented in chapter dealing with building materials.

In the transportation sector (cars, trains, trucks – but not aeroplanes !) BFRs are used in foams (PUR see chapter 4.3), electronic and electrical systems such as printed circuit boards (see chapter 4.2.), cushions and interior textiles (see chapter 4.1).

BFRs can be also found in films, video tapes and packaging materials. Expanded polystyrene (EPS) is widespread used as packaging for fragile equipment. EPS packaging for electronic equipment may contain HBCD as flame retardant. [4] Uses for these purposes are very limited comparing to others.

5. BFR- containing Products and Waste Streams

5.1 Finland

There aren't any detailed studies on BFR streams in products and wastes in Finland, although some estimations and BFR flow analyses have been made in other Nordic countries (see Chapters 5.2 and 5.3), which can be useful also in estimating BFR volumes in Finland. In order to estimate BFR streams in Finland there are couple of methods available. Possible methods could be using reports of TUKES (Finland's Safety Authority), reporting several flammability tests with electrical and electronic equipment [18, 19], and estimations from trade statistics shown in Figure 8.

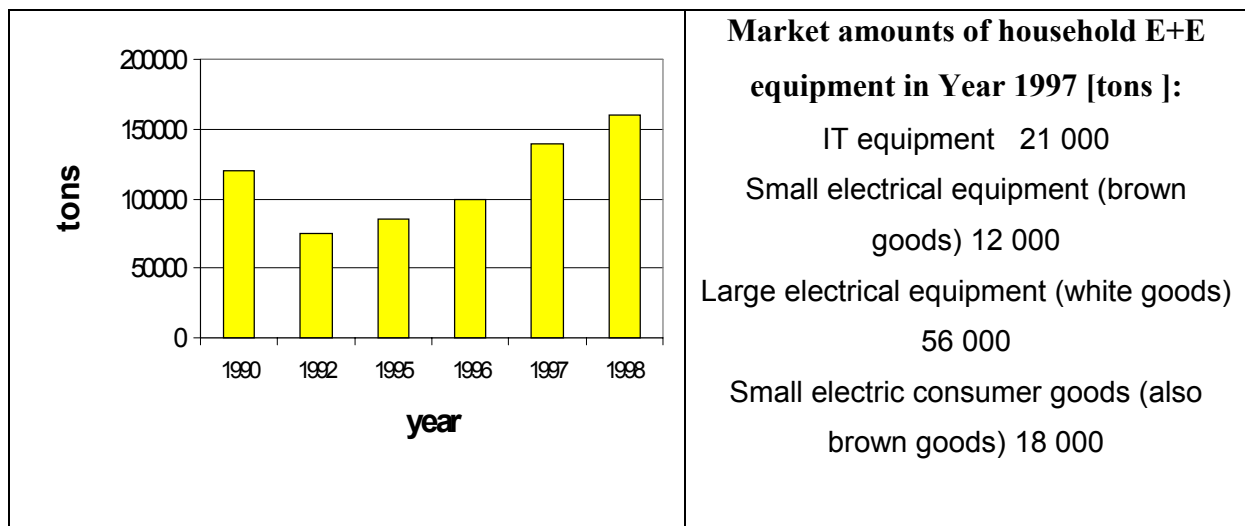


Figure 8 Electric and Electronic imports in Finland and market amounts of most of them (excluding household or entertainment goods such as control and laboratory equipment). [20]

Basically according to TUKES FTIR measurements in [19] no HBr emissions were detected in fire safety measurements of randomly chosen TV, refrigerator, dishwasher and washing machines. HCl was found from dishwasher and refrigerators.

Other useful sources are Statistics Finland's lists of wastes from production and consumption that gives estimates for potential BFR applications, e.g. for year 1997: discarded electronic equipment 411 tons from industry (excluding transformers and capacitors containing PCB or

PCT) and 3 tons from households. Undefined waste from electric and electronic industry 4 tons. [21]

5.2 Sweden

In 1998 the National Chemicals Inspectorate (KemI) was commissioned by the Government to investigate how best to phase out the brominated flame retardants PBDE and PBB. On 15 March 1999, KemI submitted a proposal to prohibit the use of PBDE och PBB. PBDE is not manufactured in Sweden but is imported and used in cables of rubber, for instance. The largest amounts are contained in imported electronic components and included in, for example, computers, tv-sets and cars. Before 1990, PBDE was also used in Swedish textiles. Today, it may occur in imported textiles and upholstered furniture. Neither is PBB manufactured in Sweden, but may be included in imported products containing electronics. [22] In Table 11 the import of brominated flame retardants to Sweden is presented.

Table 11. Import of brominated flame retardant to Sweden in metric tons. [10]

Year	1993	1994	1995	1996	1997	1998
PBDE	22	90	20	79	123	41*
HBCD	50	80	90	83	125	89
TBBPA	488	450	258	291	303	269

* Only DeBDE – containing products were imported

The World Health Organisation (WHO) has called for PBDEs “not to be used where suitable replacements are available” [6]. The PBDEs are currently moving slowly out of the EU's existing chemicals processing, but Sweden is pushing towards a ban on PBBs and PBDEs within 5 years. [10]

The Swedish Chemicals Inspectorate have produced a report on ”Phase-out of PBDEs and PBBs”, available on the internet. [23]

5.3 Denmark

In Denmark a extensive report on BFRs has been made. The report was published in year 1999 and contains detailed mass and product flow analyses of BFR streams. Import, export

and production of brominated flame retardants as chemicals according to the trade statistics from Statistics Denmark are shown in Table 12. The statistic data include the high volume aromatic brominated flame retardants as PBDEs, TBBPA and TBBPA derivatives. The net supply of these compounds in 1997 totals 29 tonnes. [4]

Vinylbromide is not included in table 11 as this compound in the statistics is registered under the same commodity position as dibromoethane that is used in high quantities as gasoline additive. [4]

Hexabromocyclododecane will be registered under the commodity position "Halogen derivatives of other cycloalkanes, -alkenes -terpenes". The Danish import and export of these chemicals was 0 tonnes in 1997. [4]

Other brominated flame retardants may be registered under commodity positions including other halogenated compounds, but it is supposed that the compounds included in Table 12 represent the major part of the supply of brominated flame retardants. [4]

The chemicals are used for compounding in Denmark. According to information from compounders it is estimated that most of the flame retardants used by compounders are reexported with compounds and masterbatches.[4]

The net supply of bromine derivatives of aromatic ethers, including the PBDEs, has decreased from about 20 tonnes per year in the period 1993-1995 to around 1 tonne in 1997 (Figure 9). The decrease in the supply of PBDEs is in accordance with the general trend in the use of these substances. [4]

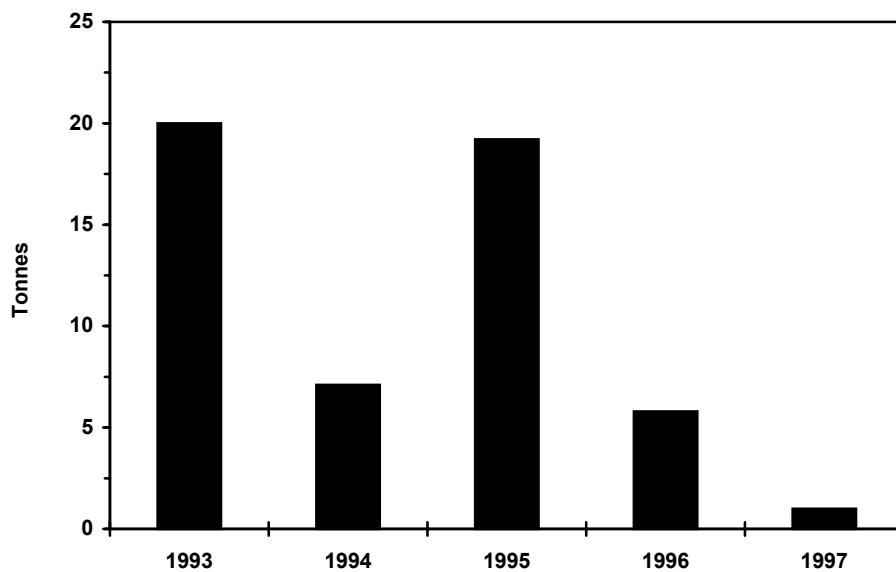


Figure 9 Import of brominated flame retardants with plastic compounds and masterbatches for production in Denmark 1997. (picture taken from [4])

Table 12. Import, export and production of brominated flame retardants as chemicals according to the trade statistics from Statistics Denmark. [4]

Flame retardant	Supply Tonnes	% of total	Supply Tonnes Br ²⁾	Plastic
TBBPA and derivatives	34-42	24	20-25	PBT, UPE, ABS, PET
PBDE	0.1-0.2 ³⁾	0.09	0.08-0.2	PE
PBB	3.3-4.9	2.6	2.8-4.1	PBT, PET
HBCD	6.1-13	6	4.6-9.8	HIPS, EPS
Brominated polyetherpolyol	80-120	63	26-38	PUR
Other BFRs ¹⁾	6	3.8	3.6	UPE, PA
Total (estimated)	130-190	100	57-81	

Notes:

- 1) Includes brominated polystyrene and dibromopentyl glycol.
- 2) Bromine content is calculated assuming a bromine content of TBBPA and derivatives of 59% (TBBPA) and of other BFRs of 60% (correspond to polybrominated polystyrene).
- 3) Decabromodiphenyl ether, DeBDE

5.4 EU

In contrast to the WHO and Sweden, the UK Department for Trade and Industry published a report claiming that concerns about these chemicals were “chemical paranoia or chemophobia”. [24] The EU is currently drawing up proposals that will ban the use of PBDEs and PBBs in electrical equipment [22], these proposals are being fought by the American Electronics Association [70]. The EU ecolable already excludes brominated flame retardants and Dell Computers intend to comply [71]. Both NEC and Philips are working on replacing BFRs [72, 73].

5.5 USA

The quantity of bromine sold or used in the United States according the Chemical Market Report 1999b was 239 million kilograms and end uses are as follows: additives and oilfield completion fluids, 20%; agricultural chemicals and fumigants, 22%; communications, construction, electronics, textiles application and transportation 28% and halons, pharmaceuticals, photography, rubber and water treatment, 30% in year 1998. The flame retardants’ part of bromine primary use was 40%. [25]

5.6 Japan

Europe’s attitude towards halogen flame retardans has also affected the Japanese, because the companies who produce flame retardant and electrical export goods to Europe are worried about regulation changes which would cause a ban on halogen-based FRs. Table 13 gives estimated amounts of flame retarded plastics in year 1997.

Table 13. Estimated amounts of flame retarded plastics in year 1997 in Japan [tons]. [26]

	PS	ABS	PC/ABS	PPE	Total
Total production	1 300 000	440 000	22 000	100 000	1 862 000
In flame retarded plastics	92 000	83 000	22 000	100 000	297 000
%	7.1	18.9	100	100	16

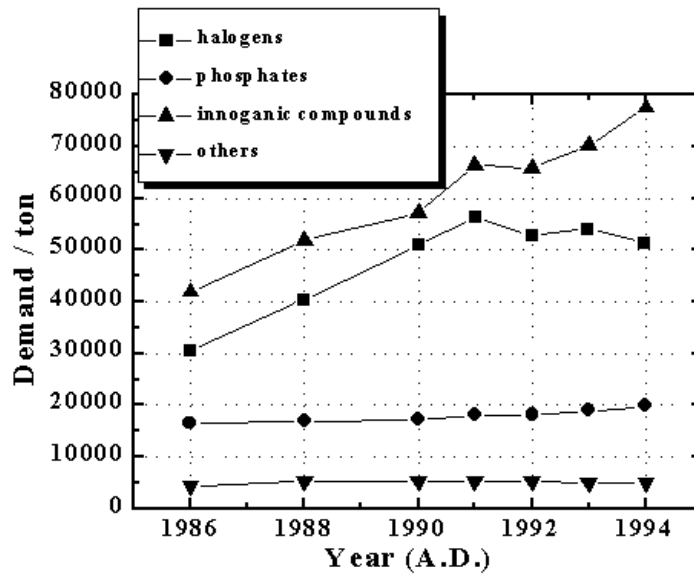


Figure 10. Consumption of different flame retardants in plastics in Japan. (picture taken from [25])

In Japan's market size of plastics as mentioned in Table 13, the rapidly growing amount PC/ABS co-polymers is not shown. The demand of flame retarded plastics has been increasing: bromine chemicals has the largest market share and phosphorous compounds, inorganic materials and chlorine compounds follow. Bromine chemical consumption has gradually decreased and phosphorous compounds consumption increased accordingly. Both changes have been slight, however, as plotted in Figure 10.

5.7 BFR markets world wide

Brominated flame retardants are produced by a few manufacturers only. The world's major BFR manufacturers are Great Lakes Chemical (USA), Albemarle Corporation (USA) and Dead Sea Bromine Group (Israel). More than 70% of the market in the USA and Western Europe is held by these companies. [4]

Because there isn't yet legislation that demands register material volumes of brominated flame retardants, most market analyses are assumptions based on market studies by commercial companies such as Frost & Sullivan, country's environmental authorities, or

statistics from manufacturers or coalition or forums of them, such as Bromine Science and Environmental Forum (BSEF), Brominated Flame Retardant Industry Panel (BFRIP) and European Flame Retardant Industry Panel (EBFRIP).

Table 14 lists major brominated flame retardants estimated market volume by region. Because market volumes are estimates one can find conflicting amounts when comparing these statistics to numbers given in Chapters 5.5 and 5.6. Still, however, markets are strongly situated in high-tech Asian countries such as Taiwan and Japan. In Japan and the USA there are much stricter fire safety regulations than in Europe and in Europe the demands for replacing BFRs by non-halogen FRs have a much longer history than in United States and Japan.

Table 14. Major brominated flame retardants estimated market volume by region (1999). [27]

[tonnes]	Americas	Europe	Asia	Total
TBBPA	21 600	13 800	85 900	121 300
HBCD	3 100	8 900	3 900	15 900
Deca-BDE (DBDPO)	24 300	7 500	23 000	54 800
Octa-BDE (OBDPO)	1 375	450	2 000	3 825
Penta-BDE (PBDPO)	8 290	210	--	8 500
Total	58 655	30 860	114 800	204 325
Region's market share	28.7%	15.1%	56.2%	

6. Legislation

There are two types of legislation affecting the flame retardant industry, being fire regulations and environmental regulations. Sometimes, these two are in conflict.

Flame retardants play an important role in protecting life and property. Interest groups, such as the Alliance for Consumer Fire Safety in Europe (ACFSE) are well-organised and effective in raising fire safety awareness. As a consequence, more stringent flammability standards are being introduced. Different kinds of flammability tests are being standardised and products have to pass strict fire safety tests and measurements before product sales are permitted. This has resulted in a greater demand and changing requirements for flame retardants, favouring low smoke and fume products.

Concern over the environmental impact of BFRs arose for the first time in 1973 when a commercial flame retardant containing PBBs was accidentally mixed into feed for dairy cattle, livestock and poultry in the state of Michigan, USA. The feed was used widely, leading to widespread PBB - contamination of milk, meat and eggs, and poisoning of animals. Over 9 million people were exposed to PBBs from food. Because of this widespread exposure, the research was funded to improve the understanding of the toxicology of PBBs, and poisoned animals and exposed humans have been studied as well. The effects of PBBs were found to be essentially the same as those seen for PCBs.[10]

The most recent European Commission proposal for a directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment proposes the substitution of cadmium, lead, mercury and hexavalent chromium. The same applies for two types of brominated flame retardants, being polybrominated biphenyl ethers (PBDE) and polybrominated biphenyls (PBB) by 2008. [28]

Besides EU directives such as the proposal for the restriction of certain hazardous substances in electrical and electronic equipment [7] and World Health Organizations Health Criteria on BFRs [6] there are several national regulations and guidelines concerning BFRs. Table 15 lists some prescribed legislation in industrialised countries.

Table 15. Survey of national activities concerning regulation, soft regulation, risk and hazard assessment activities and national positions on the issue of brominated flame retardants. [4]

Country	Action – regulation	Action - soft regulation	Risk / hazard assessment	National position
Austria	PBB and TRIS: manufacture, supply, import and use of compounds as chemical or preparation are banned ¹⁾			Supports international regulation of PBDE and BFRs in general
Belgium	No specific actions have been taken to ban certain uses of selected BFRs or to implement major measures to control, limit or reduce their risks (1994)			Awaits an international strategy
Denmark	PBB ²⁾ and TRIS ^{2), 3)} are banned in textiles, respectively textiles with skin contact	BFRs are on the Danish List of Undesirable Substances	The present substance flow analysis and assessment of alternatives 1998/99	Restrictions on these substances are desired because of their diffuse distribution in the marine environment
Finland	PBB banned in textiles with skin contact ²⁾			Supports international restrictions on the use of BFRs
France	PBB banned in textiles with skin contact ²⁾		Undertakes jointly with the UK risk assessment of OcBDE and DeBDE ⁴⁾	
Germany	Prohibitions on products contaminated with PBDDs/PBDFs Regulation on producer/importer's responsibility at the waste stage	Voluntary substitution of halogenated compounds	An investigation of flame retardants at the German market is planned to be finished year 2000	PBB and PBDE must be banned
Japan		Voluntary phase out of PBB, hexaBDE and tetraBDE		DeBDE is considered as a highly safe chemical
The Netherlands	Promulgation of regulation of PBB/PBDE was in 1994 on hold	Voluntary reduction of use of BFRs in end products	National risk assessments of PBB and PBDE in 1991 and 1994	There is a strong preference for international measures

Table 15. (..... continued)

Country	Action - regulation	Action – soft regulation	Risk / hazard assessment	National position
Sweden	PBB and TRIS banned in textiles with possible skin contact ²⁾	The Swedish Government states that: PBB and PBDE will be phased out and the use of other BFRs should be limited Voluntary substitution in textile and telecommunication industries	Sweden has assigned HBCD for risk assessment in the EU ⁴⁾	Special attention is devoted to PBDE and PBB
Switzerland	PBB and PBB containing products: manufacture, supply, import and use are banned			Advocate for a phase out of PBDE
United Kingdom	TRIS and PBB are banned in textiles with possible skin contact ²⁾		Undertakes jointly with France risk assessment of OcBDE and DeBDE. Has assigned PeBDE for risk assessment ⁴⁾	
United States	No action	1979: Voluntary phase out of PBB	Under way: Risk assessments of: 1. dioxin/furan contamination's in substances, 2. hazard potential of selected substances, 3. dioxins/furans from manufacture/com-bustion	1994: No national position on BFRs
Norway	PBB and TRIS banned in textiles with possible skin contact ²⁾	The release of BFRs must be significantly reduced before the year 2010	An investigation of the domestic flow of BFRs is planned to be carried out in 1999	
Italy		Voluntary substitution of halogenated compounds through implementation of internal industrial standards ⁴⁾		

1) Austrian ordinance BGB1.No.210/1993

2) Implementation of EC Dir. 76/769

3) Danish ordinance No 1042, §16/ 14-12-95 / 17-12-97.

4) Risk assessment of existing substances, regulation 793/93/EE

5) Examples are the following internal standards adopted by: ENEL – National Agency for Electric Energy – and FS – National Railway – (CEI 20-37 standard); Milan City Underground (standard based on Sheet G 8998); and Marina Military (NAVI 3A075 standard). The achievement of these standards tends to exclude the use of halogenated flame retardants.

7. Treatment of wastes containing brominated flame retardants

Increasing environmental awareness is deeply affecting end-of-life management systems for wastes containing BFRs. Attention focusses specially on waste management of electric and electronic equipment basically for two reasons: WEEE streams include significant amounts of precious metals such as copper, gold, silver and platinum and secondly these equipment are the most important application of BFRs. European legislation is moving strongly toward waste management systems addressing products that contain hazardous substances. There are basically three ways to recycle products: to recycle the product itself, to recycle materials into new products and to recycle the energy content of the product.

For many waste streams recycling routes may be blocked due to the presence of BFRs. For example, the use of recycled ABS (acrylonitrile-butadiene-styrene) as a blend with PC (polycarbonate) is not possible because the BFR causes the PC to depolymerise, resulting in poor quality of the recyclate [30]. Feedstock recycling, *i.e.* the recovery of organic chemicals or precious metals from waste streams that contain BFRs may partly be accomplished by mechanical methods although it is recognised that, for example for WEEE, thermal methods are generally more powerful [30]. Also, there is a large interest from the bromine industry to recover bromine from waste streams that contain BFRs by means of thermal treatment [31-32]. Most important examples here are DecaBDE found in HIPS (high impact polystyrene) in brown goods and TBBPA used in ABS in data processing and office equipment as well as in epoxy resins in printed circuit boards [32].

7.1 Mechanical recycling (of waste streams such as WEEE)

Mechanical processing and recycling of BFR-containing waste streams such as WEEE may be accomplished by selective disassembly, shredding, magnetic and eddy current separation as to so generate metal-rich fractions. The final stage produces an aluminium fraction and a copper concentrate containing precious metals and combustible plastics [29]. A typical mechanical recycling plant's is based on a magnetic separator (iron, magnetic steel) and a vibrating separator (for light fractions such as plastic and glass). For the rest of the metals there is the possibility of manual sorting or different kinds of more specified and expensive procedures such as eddy current separation for aluminium and flotation techniques, for example for copper and zinc.

7.2 Thermal treatment of bromine-containing wastes: general aspects

7.2.1 Contamination by BFRs and recovery / recycling

During recycling or recovery contamination presents itself in a many forms such as dirt, partially oxidized polymers, printing inks, paper, pesticides, metals and additives such as flame retardants. The potential for undesirable/antagonistic interactions and the probability of undetected contamination being present, eventually leading to a reduction of the recyclate quality, is high. [33]

Even if manufacturers could allow certain amount of impurities in recycled products another problem lies with always changing additive characteristics and amounts. Basically the same kinds of products could have completely different impurities now than 20 years ago. Of course one may assume an average useful life of different consumer products such as upholstered furniture, electronic and electrical products and so one. In addition to this, some BFRs (most importantly PBB) have been banned due to potential toxic hazards recognised in certain countries and it may be even legally impossible to recycle them. Contamination by flame retardans is one of the most important factors that effect the recyclability of polymers.

The fate of bromine in thermal treatment has come more urgent through recent WEEE recycling directive because it forces to recycle more WEEE than what is possible with mechanical methods.

Thermal processing of the copper concentrate with high contest of precious metals, generated by mechanical processing end-of-life electronic and electronic equipment (EEE), is currently the most cost-effective and proven means to recover copper, precious metals and some energy and at the same time achieve destruction of some hazardous substances. [29] The major concern is the formation of brominated dioxins and furans but also HBr, Br₂ and non aliphatic compounds emissions must be investigated. There is a possibility to recycle flame retarded polymers, “at least under certain experimental experimental conditions” according to Riess *et al.* [34].

7.2.2 *Recovery of bromine from bromine-containing wastes*

It is also possible to recover bromine from WEEE in economically and ecologically feasible way: the isolation of the bromine from the gas stream in a suitable form for reuse is based on absorption into an aqueous (hydroxide) solution. The hydrogen bromide in the product gas may be neutralised and converted into salt. Also a hydrobromic acid solution could be produced as an end product. The bromine salts or residues are converted by the bromine industry into bromine products, thereby closing the bromine loop. [31]

Upon incineration, combustion or gasification the bromine from brominated compounds will distribute over bottom ash, fly ash and flue gas. Around 78% of the bromine was found in the gas phase after combustion on a grate, while the other 20 % and 2 % were found in the fly ash and grate ash, respectively [35]. Similarly, pyrolysis of two types of WEEE at 550°C followed by gasification with oxygen at >1230°C [31] resulted in a bromine release of 20-98 % to the gas phase. Under these conditions the most important bromine compound is HBr, with small amounts of Br₂ and possibly metal bromides [31, 35-36]. The recovery of this is accomplished either as HBr by adsorption in water (at pH=1) or by neutralisation with sodium or calcium hydroxide, forming NaBr or CaBr₂, where first process appears more feasible from a bromine-recycling point of view [31,32,35].

These processes involve the risk of Br₂ emissions from the scrubber that would need further processing, whilst also the reaction $\text{Cl}_2 + 2\text{HBr} \rightleftharpoons 2\text{HCl} + \text{Br}_2$ may take place when large amounts of chlorine are present, which shifts to the right-hand side with increasing temperature. When also antimony (Sb) is present (as is always the case with PBDE-type BFRs) SbBr₃ may form, which will be oxidised or hydrolysed to Sb₂O₃ and HBr at lower temperatures [35].

A recent study by the APME, Forschungszentrum Karlsruhe and EBFRIIP [28,37] addressed the options for WEEE co-firing in a municipal solid waste (MSW) combustor, at the same time aiming at the recovery of bromine. The TAMARA facility at Karlsruhe was used. WEEE fractions considered were shredded TV housings, shredded printed circuit boards and several others. It was also here found that up to 90% of the bromine enters the gas phase, although 25 ~ 40 % of the bromine from the TV set housings was found in the fly ashes. The HBr was recovered from the flue gas using a scrubber operating at pH 1 or lower. Besides HBr, the

presence of Br₂ was observed when the total bromine concentration gas phase was above ~300 mg/m³. This was found to correlate with SO₂ concentration: the formation of Br₂ is followed by the oxidation of SO₂ to SO₃ via the reaction $\text{Br}_2 + \text{SO}_2 + \text{H}_2\text{O} \rightleftharpoons 2 \text{HBr} + \text{SO}_3$ [28], as illustrated by Figure 11.

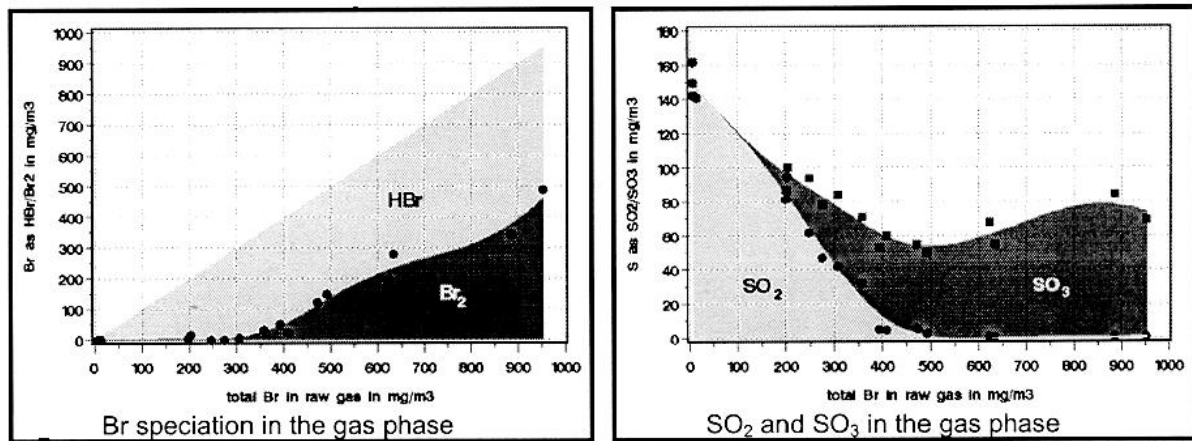


Figure 11 Speciation of bromine and sulphur in the gas phase during the TAMARA tests (picture taken from [28])

The removal of Br₂ from the flue gases is not straightforward but was accomplished by adding Na₂S₂O₃ to the second scrubber, which operates at pH around 7 (mainly for absorbing SO₂). Also it was found that the volatilisation of metals is increased by the presence of bromine, similar to the effect of chlorine [49], resulting in increasing amounts of Cu, Zn, Sb and Pb in the fly ash [37]. Altogether it was concluded that 2-3 %-wt WEEE containing ~2.5 %-wt brominated flame retardants can be added to the MSW combustor feed, allowing at the same time for the recovery of ~90% of the bromine. Preferably the bromine is recycled as a 48 % HBr solution. Depending on the presence or availability of chlorine (to extract Br₂ from NaBr) on the site, the quality of the WEEE and market conditions for HBr, NaBr or Br₂ the most suitable route for recycling of bromine from WEEE are given in Figure 12 [37].

During pyrolysis of scrapped electronic circuit boards, it was reported by others that ~72 % of the bromine was released to the gas phase, mainly as bromobenzene, C₆H₅Br, and HBr [14]. Several researchers working on the pyrolysis of BFRs or BFR-containing materials have found no or only trace amounts of HBr in the product gases, finding methyl bromide (CH₃Br), ethyl bromide (C₂H₅Br) and propyl- and propylene bromide (C₃H₇Br and C₃H₅Br) instead [15,38,39,44].

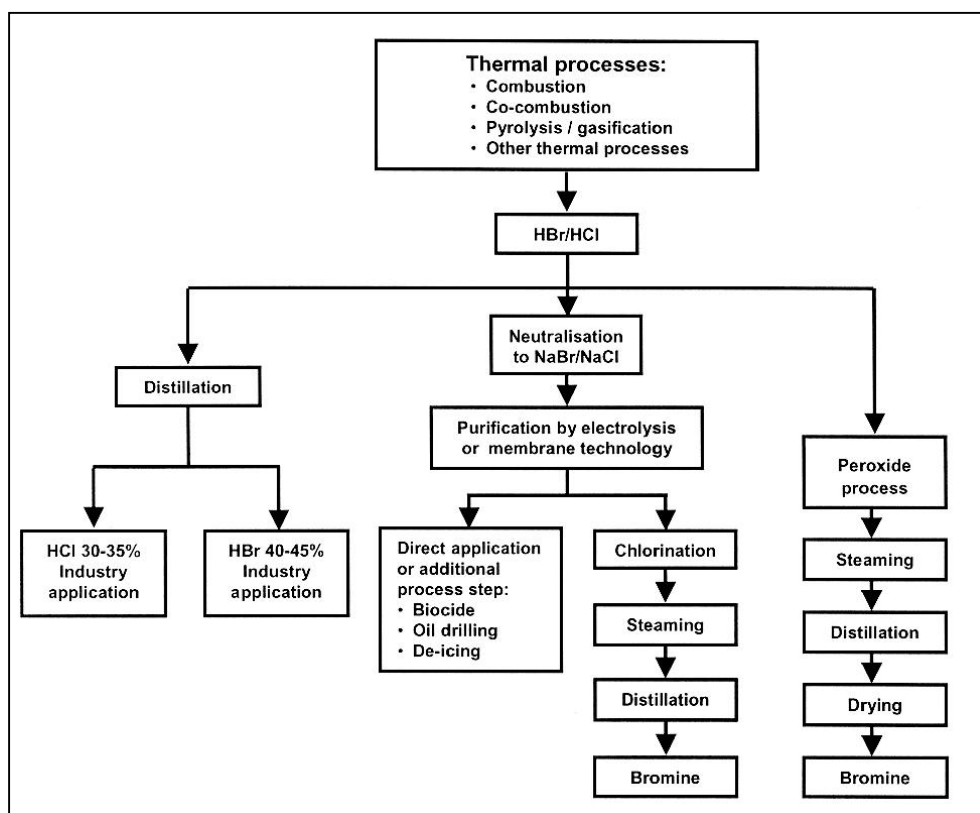


Figure 12 Options for bromine recovery from WEEE (picture taken from [37])

7.3 Thermal treatment of bromine-containing wastes: processes

For the thermal treatment of waste streams that contain significant amounts of BFRs there are basically as many behaviour paths as there are different BFRs because their chemical properties are very different.

Basic thermal treatment methods are combustion or incineration, gasification and pyrolysis from which the combustion is the most common. Grates or stokers, rotary kilns and circulating fluidised beds (CFBs) are typical furnace types for thermal treatment for waste. Rotary kilns are widely used to incinerate hazardous waste, grate furnaces are generally the first choice for mass burning of municipal wastes. At the same time, CFBs are increasingly being used for the co-firing of refuse derived fuels (RDF) usually with another fuel such as coal, peat or biomass. All these methods are suitable for making use of the energy content of organic part of waste, *e.g.*, the plastics fraction in computer monitor housings. Recycling of the energy content of an end-of-life product is also accepted in the EU's latest WEEE

recycling directive [7] and after a thermal treatment the inorganic rest fractions are easier to process with a mechanical recycling process.

7.3.1 Rotary kiln furnaces

A rotary kiln is very suitable for process where one option is material recovery. In an ideal case, plastics and other organic compounds vaporise to the flue gases and for example precious metals remain in ashes that are easily removed from the furnace. A basic working scheme of a rotary kiln is given in Figure 13.

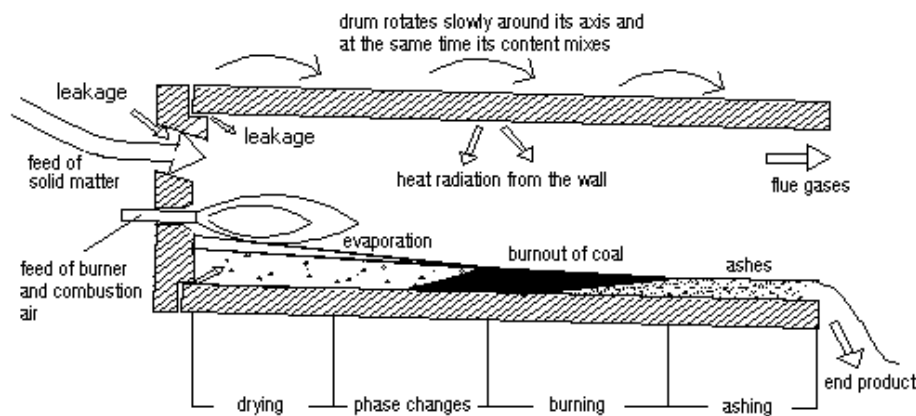


Figure 13. A Rotary Kiln.

Usually the working temperatures in kiln processes are above 1000°C but in metal recovery processes temperature should be significantly lower because of the melting points of recoverable metals. Because the most important metal in E+E waste is usually copper, the kiln temperature shouldn't rise above 700°C.

7.3.2 Mass burning on a grate

Mass burning on a grate, or stoker, is the most conventional way to accomplish waste incineration. This system isn't the best option for material recycling because the quality input varies much.

Pilot scale tests simulating conditions of typical MSW incineration plant were carried out at Karlsruhe. The test's input was combination of "typical" MSW besides a Br content of waste was 100 times higher than usual. Addition of Br didn't have negative influence upon the

combustion performance and 60-80% of the input's Br inventory was released into the raw gas. [16] (see also section 7.2.2)

7.3.3 Fluidised bed reactors

There are two basic types of fluidized-bed furnaces, circulating and bubbling. Basic idea in both is the same: lower parts of furnace are filled with solid particles which are set into motion (= fluidization) by blowing a gas stream upward through the bed. Under the influence of the gas stream the bed acts like boiling liquid. The bed's mass is significantly higher than the fuel's mass which offers the possibility to feed in fuels with varying moisture and heat value content. The bubbling bed mixes fuel well and heat transfer between fuels solid and gaseous phases and bed's solid particles and furnace walls is good. Figure 14 presents a circulating fluidized bed plant, which is designed for the combustion of recovered fuels.

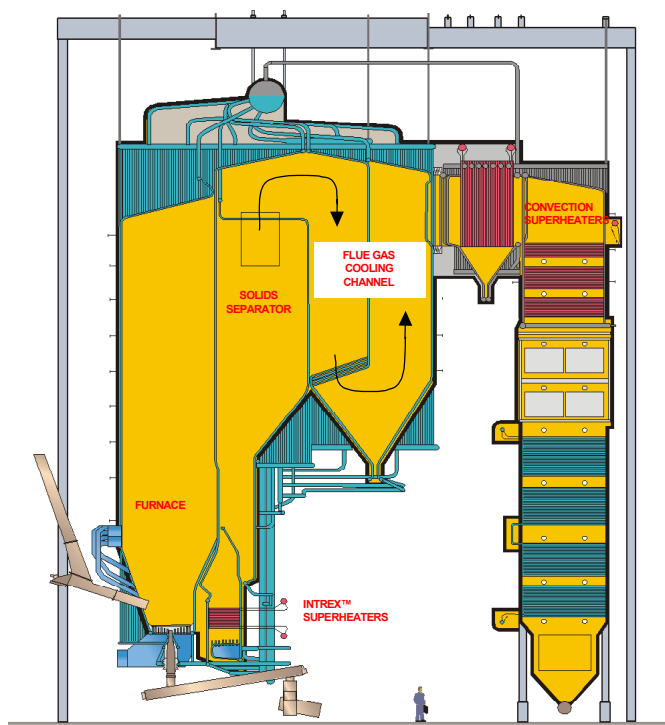


Figure 14 CFBC-plant at Högdalen, Sweden. (picture taken from [40])

Because the halogen (typically chlorine) content of fuel the inner heat transfer surfaces are located after flue gas cooling channel and in the solids return in order to avoid high temperature corrosion.

7.3.4 Pyrolysis drums and other pyrolysis systems

There are several different kind of pyrolysis systems designed for thermal treatment of waste. Some of those applications have already in full scale plant size and they are in commercial use. One of those systems is the Japanese R21 system (see Figure 15) which can handle even 150 000 tonnes of MSW per annum (depending on plant size).

Benefits of this kind of system, from a material recycling point of view, are that because the furnace is drum- like the residue doesn't agglomerate and block furnace so easily as in other types of furnaces and metals don't oxidise because of the lack of air. The drum is heated outside with heat coming from high temperature combustion chamber and the temperature inside the drum is about 400°C. After organic fractions have been vaporised in the drum and flue gases lead to high temperature combustion chamber and burned. Organic residue is separated from inorganic and fed also to a high temperature combustion chamber. Because the reducing conditions in pyrolysis drum and later high temperature burning of pyrolysis gas, the amount of PCDD/F compounds (and probably also PBDD/F compounds) are very low.

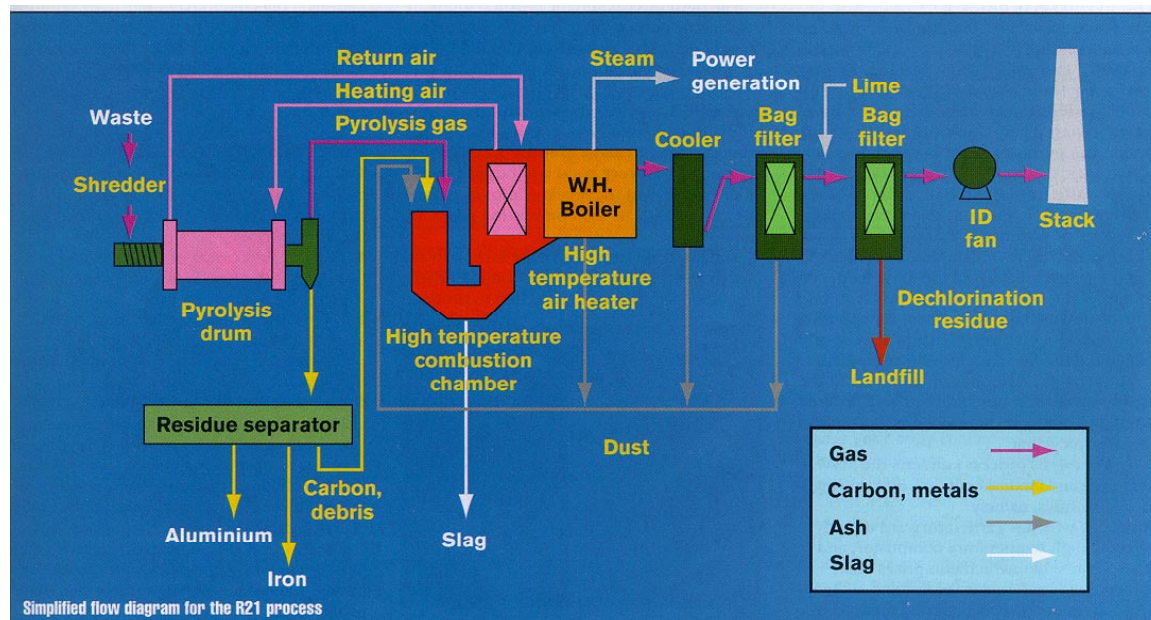


Figure 15. R21 Pyrolysis process. (picture taken from [41])

There are various other possibilities for pyrolysis reactors such as basic gasifier type of solution where the gasifier is externally heated without oxidising conditions inside the reactor. In this kind of system inorganic fractions can block inside the reactor. A possible pyrolysis reactor is a bubbling fluidized bed in which the fluidizing gas is nitrogen. One of the variations of this kind of system is studied (primarily for the combustion of high-PVC solid waste with HCl recovery) at the laboratory of Energy Engineering and Environmental Protection at Helsinki University of Technology [42, 44].

7.4 *Formation of Brominated Dioxins and Furans During Thermal Processing of BFR- containing Wastes*

Besides the possible environmental and health hazards caused by certain BFRs during their production, their use in processes and or product life, a major point of concern is that polybrominated – p- dibenzodioxids and dibenzofurans (referred to as PBDD/Fs) are formed during thermal processes such as waste incineration. Indeed, brominated dioxins and furans (PBDD/Fs) can be formed according to chemical routes similar to their chlorinated PCDD/F analogues: also here the *de novo* formation route during cool-down of gases is important [43].

Very little is known about the toxicity of PBDD/Fs [24] although the WHO reports it to be “more or less similar” to the corresponding PCDD/Fs [45]. Also, in many cases the PBDD/Fs are accompanied by halogenated polyaromatic hydrocarbons (PAHs) that pose a greater risk [24]. One aspect that must not be forgotten is that many chemicals like bromophenols and BFRs such as PBDE and TBBPA are contaminated by small amounts of PBDD/Fs during their production [45]. It is therefore not surprising that often the amount of PBDD/Fs formed during thermal processing of BFR-containing materials is smaller than the amount that is destroyed, *i.e.* the process acts as a sink for PBDD/Fs [43, 46].

When compared to the “more common” PCDD/Fs the PBDD/Fs are characterised by higher molar masses, lower melting points, lower vapor pressures and lower water solubilities. One important difference is the high sensitivity to photolysis, *i.e.* destruction (bromine removal) under the influence of light: lifetimes for PBDD/Fs may vary from less than one minute in the

atmosphere to several months in soils. PBDD/Fs are generally found in the atmosphere bound to particles. As with PCDD/Fs, the formation of PBDD/Fs during thermal treatment of BFR containing polymers is depending on oxygen, polymer types, temperature and additives such as Sb_2O_3 . The latter may bring down the temperature window where PBDD/Fs are formed from typically 600-900°C to as low as 400°C. When also chlorine is present, mixed halogen congeners $\text{Cl}_x\text{Br}_y\text{DD/Fs}$, also referred to as PXDD/Fs (X=F,Cl or Br) may be formed [45].

Sakai *et al.* [43] reported that the presence of metals such as Fe and Cu promotes the formation of PBDD/Fs, whilst the ratio of PBDDs to PBDFs decreased with increasing chlorine concentration.

For flame retardants such as polybrominated diphenylethers (PBDE) the chemical routes to PBDD/Fs are very short, as seen in Figure 16 [47]. Zelinski *et al.* reported measured concentrations of ~ 15 ppmw in deposits near a burned-out TV set after a residential fire [48]. Adding approx. 5 %-wt of PentaBDE to a municipal solid waste burnt in a German incinerator yielded concentrations of 0.4-0.6 mg Br/kg as PBDD/F in fly ash removed by the electrofilter [24].

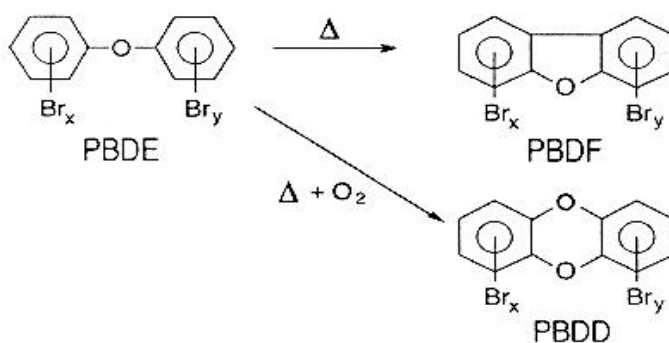


Figure 16. Formation of PBDD/Fs from PBDE flame retardants $x+y=5,8$, or 10 (picture taken from [47]).

Experiments made during the mid 1980s showed that up to 10% of the bromine from PBDEs can form PBDD/Fs when heated to 510-630°C [51]. Somewhat later similar results were presented for the range 600-800°C, with the tetra- and penta-bromo substituted compounds as the most “abundant” homologues, whilst for the other BFRs much smaller amounts of PBDD/Fs were found after pyrolysis of polymers containing these compounds [52].

The risks for PBDD/F formation is one reason why PBDE and PBB-type flame retardants are more and more replaced by TBBPA or non-halogen flame retardants. As mentioned above, Riess *et al.* [34] recently reported that PBDE are still found in polymers from electrotechnical applications. Also very recently Wichmann *et al.* [50] analysed the formation of PBDD/Fs from TBBPA in air at 600°C and found that amounts formed were not large (of the order of 20 mg PBDD/Fs /kg TBBPA) but not zero.

For lower temperatures, Hamm *et al.* [64] recently grounded and injection-molded (temperatures up to 600 K) a HIPS polymer containing DeBDE and Sb₂O₃ repeatedly (5 times) as to simulate sequential recycling. Not more than 5 ppb total for the eight regulated PBDD/F congeners was found.

As for the mixed brominated/chlorinated PXDD/Fs: recent work in Sweden on MSW samples with BFRs in a fluidised bed combustor (FBC), showed for the three BFRs TBBPA, DeBDE and HBCD, that CO emission levels in the flue gas were increased while SO₂ levels decreased with BFRs present in the fuel [61]. This corresponds to findings at Karlsruhe, showing that SO₂ is oxidised to SO₃ (see Chapter 7.2.2). At the same time, PCDD/F concentrations decreased somewhat, although tetra-BDD/Fs were found, which were formed apparently along the same routes as the tetra-CDD/Fs. Most abundant, though, were the mixed Cl_xBr_yDD/Fs, showing for their relative amounts a Gaussian distribution from (x=4, y=0) *i.e.* tetra-CDD/F, to (x=0, y=4) *i.e.* tetraBDD/F, peaking at (x=2, y=2), *i.e.* dichlorodibromo DD/Fs. No BFRs were found in the flue gas. It was suggested that the species BrCl is present in the gas in significant amounts at temperatures up to 700°C, which affects the PCDD/F formation via the reaction $\text{Br} + \text{Cl}_2 \rightarrow \text{BrCl} + \text{Cl}$ [61].

Similarly, also in the US recent studies [62] showed that brominated organic species present in the feed of a chlorinated waste incinerator may reduce PCDD/F emissions by as much as 30% at a Br/Cl molar ratio of 0.1 in the feed. In this case, despite experimental limitations (lack of calibration standards!) three “larger” PXDFs were detected: Cl₆BrDF, Cl₅Br₂DF and Cl₇BrDF. Another finding was that with bromine present, the presence of chlorobenzene in the flue gas shifted to the presence of bromobenzene.

8. On-line and Off-line Analysis Techniques for Identification and Concentration Measurement of Brominated Chemicals in Waste Streams and Gases

For the detection and quantitative analysis of brominated chemical compounds in waste streams and in the exhaust gases and solid residues from thermal treatment processes two methods are the most important: mass spectroscopy (MS) and infrared analysis (IR). Besides these, several wet-chemical and other methods are used as well. The analytical methods for the characterisation are listed in Table 16 [34].

Table 16. Analytical methods for the characterisation of halogen and polymer samples.

Analytical method	Purpose
Infrared spectroscopy (FT-IR) in combination with thermogravimetric methods	Polymers
Pyrolysis gas chromatography (py-GC/MS) with mass spectrometric detection	Polymer and flame retardancy class
Energy dispersive x-ray fluorescence (ED-XRF)	Halogen containing samples
High resolution gas chromatography with mass spectrometric detection (HRGC/MS)	Quantification of polybrominated dioxins and furans (PBDD/F)

8.1 Mass spectroscopy + gas chromatography (MS-GC)

The use of mass spectroscopy takes full benefit that the halogen compounds Cl and Br occur in nature as two isotopes: Cl as ^{35}Cl and ^{37}Cl , at a ratio 3:1, and Br as ^{79}Br and ^{81}Br at a ratio 1:1. Thus, an ion containing one Br atom can be identified as a double peak at m/z (mass/charge) = M and at M+2 in an MS spectrum, one containing two Br atoms as 3 peaks with an intensity ratio 1:2:1 at $m/z = M, M+2$ and $M+4$, etc. [53]. For example, the MS spectrum of CH_3Br shows peaks at $m/z = 15$ (CH_3), 79 (^{79}Br), 81 (^{81}Br), 94 ($\text{CH}_3^{79}\text{Br}$) and 96 ($\text{CH}_3^{81}\text{Br}$). This is illustrated by the spectra given in Figure 17, for brominated compounds which have been measured in ambient air [55].

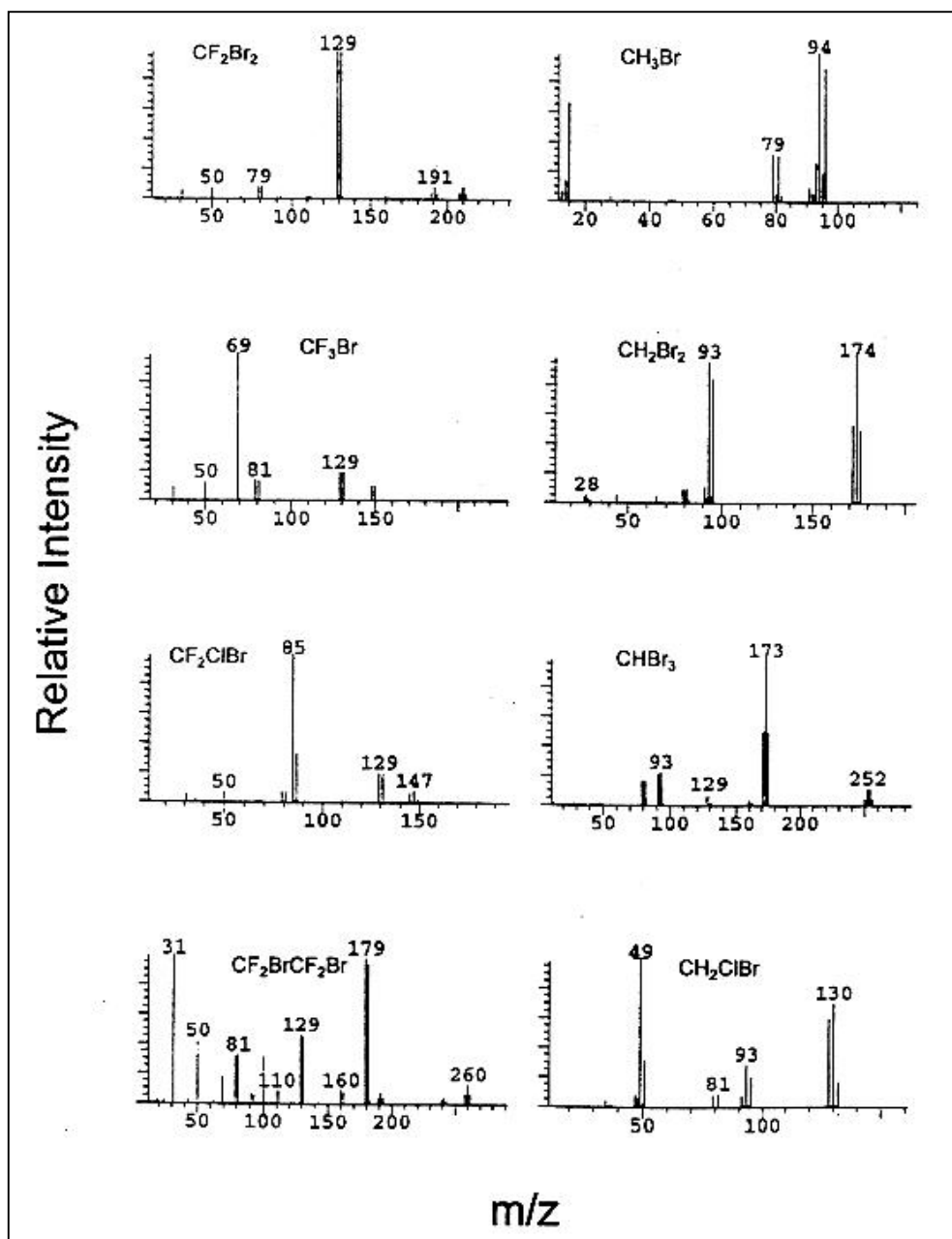


Figure 17 Examples of mass spectra of brominated species that have been detected in air samples (picture taken from [55])

A clear disadvantage of the method is the high cost and the fact that fragments of the original compound are detected which can make species identification difficult. Nonetheless, a lot of research on polymer thermal degradation, including BFRs is based on pyrolysis+gas chromatography/MS (Py-GC/MS) [14, 34, 38, 39, 51, 54]. High-resolution MS methods (GC-HRMS) can be optimised to detect brominated compounds in air at concentration below the parts-per-trillion level. For example, methyl bromide (CH_3Br) was detected at around 15 ppt in ambient air the US during Fall 1998 [55].

According to Wang [56] the combination GC + atomic emission detection, *i.e.*, Py-GC/AED has advantages over Py-GC/MS because for BFR compounds, for example, “there is no good way to know the identity of the aliphatic or aromatic counterpart to which the halogen element is attached”. The procedure applies the emission lines of carbon, hydrogen and bromine at 496, 486 and 478 nm, respectively. A specific polymeric flame retardant for example can be identified by a peak pattern after a sufficient set of calibrations is made. The analysis of a BFR within a polymer matrix are preferred over the analysis of a pure BFR.

With respect to the gas chromatograph (GC) that is used upstream of the MS analyser: in order to separate the compounds present in a mixture, standard data are a typical problem when dealing with compounds related to brominated flame retardants. This especially holds for the brominated dioxins and furanes, PBDD/Fs, not to mention the mixed Cl_xBr_yDD/Fs, for which 5020 congeners are possible. Recently correlations were reported that relate the GC retention time of PBDDs to that of the analogue PCDDs. When expressing the retention time by a capacity factor, *k*, as a function of temperature, *T*, via $\ln k = A + B/T$, it was reported by Liang *et al.* [65] that the parameters for PBDDs and PCDDs are correlated by the simple relations $A_{\text{PBDD}} = 0.506 + 1.063A_{\text{PCDD}}$ and $B_{\text{PBDD}} = -2469.1 + 1.427B_{\text{PCDD}}$, with regression coefficients $R^2 > 0.99$. This should hold for all 75 PBDD congeners. GC column temperatures used were in the range 200 - 270°C [65].

8.2 Infrared (IR) spectroscopy

Infrared spectroscopy is based on the absorption of infrared light at frequencies specific for stretching, bending and other oscillations inside molecules. Typically the frequency range from 2.5 to 25 micrometer, or wavenumber 400 – 4000 cm⁻¹ is used, although lower wavenumbers (far infrared frequencies) may also be used. Nowadays the method is always combined with Fourier transform-based signal processing procedures, referred to as FT-IR [53]. For BFRs, important frequencies are approx. 2555 cm⁻¹ for HBr, 755 cm⁻¹ for bromobenzene, approx. 3000 cm⁻¹ and approx. 1500 cm⁻¹ for methyl benzene, approx. 3100 cm⁻¹ and approx. 1500 cm⁻¹ for benzene. Also important are the frequencies for water (1300-1900 cm⁻¹ and 3500-4000 cm⁻¹) and carbon dioxide (2300-2400 cm⁻¹) [14,57]. As an illustration, the FT-IR spectrum of HBr, measured as part of the research at the lab for Energy Engineering and Environmental Protection [15,44] is given in Figure 18. One benefit of this technique is that it is nowadays available at reasonable cost, although calibration work for

“non-conventional” species such as HBr and CH₃Br requires standardised samples that may be hard to find. Also, many halogenated compounds have their “fingerprint” frequencies at low wavenumbers, *i.e.* below 800 cm⁻¹.

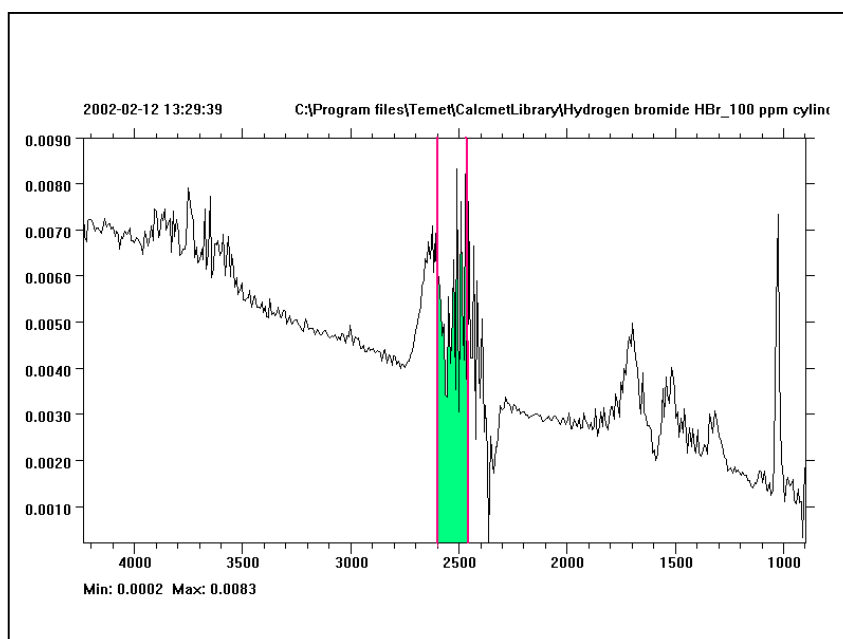


Figure 18 FT-IR spectrum for HBr (from 100 ppm HBr in N₂ mixture)

8.3 Other methods

Measurement of nuclear quadrupole moment of ⁸¹Br has been used successfully to detect how brominated flame retardants are dispersed in a polymer matrix, and to determine the crystal structure of brominated aromatic compounds. Using an NMR (nuclear magnetic resonance) spectrometer (10-300 MHz) spectral signals were obtained in the range 227 – 256 MHz with an accuracy of the order of 1 MHz. [58, 59]. This method is based on the fact that the nuclei of atoms such as ¹H, ¹³C, ¹⁹F and apparently also ⁸¹Br have a spin that gives rise to a magnetic field that can be measured [53]. Similar to mass spectroscopy methods, this method is quite expensive and especially in this case requires highly skilled personnel.

Fraunholz and van Kooy [66] very recently suggested to use X-ray transmission, similar as is being used to scan luggage at airports, for detecting heavy elements such as chlorine, bromine or heavy metals. After this, selected particles can be separated and submitted to more detailed analysis. When using a dual energy method (as modern airport scanners use) the elements detected can be further separated into several classes.

9. Summarising conclusions

Brominated flame retardants BFRs are effective at increasing fire safety of several products, mainly textiles and polymers that are used in electrical and electronic (E+E) equipment. The production of BFRs and BFR-containing products and the fact that most of these products end up in waste streams after only a few years resulted in measurable quantities of BFRs in the environment rather soon after their large-scale introduction into the market. This resulted in many sometimes very extensive studies (*e.g.* [4]) as to the effects of BFRs on the indoor and outdoor environment, followed by studies addressing the processing of BFR-containing end-of-life products (like the present report) and, most recently, the recovery of bromine in combination with BFR-containing waste processing [37]. Against a current BFR consumption in Europe of 3000 – 35000 tonnes/year, approximately 8000 tonnes of bromine may be recovered and recycled from WEEE.

After a worldwide phase-out of polybrominated biphenyls (PBBs), the polybrominated diphenyl ethers (PBDEs) are, at least in Europe, being more and more being replaced by the most important BFR nowadays: tetrabromo bisphenol A (TBBPA). The PBDE penta-BDE is to be phased out before the end of 2003 while EU risk assessments are ongoing for octa- and deca-BDE, as for TBBPA as well. At this point differences are arising between Europe and USA + Japan, where fire regulations are more tight. This will result in lower consumption or phase out of BFRs in Europe that will be widely used elsewhere, and could interfere with future international trade of BFR containing products, most importantly consumer electronics.

One potential environmental and human health hazard is formed by polybrominated dioxins and furans, in short PBDD/Fs, *i.e.* the brominated analogues of chlorine-containing, supertoxic PCDD/Fs. Not only are these present in very small amounts in BFRs and BFR-containing products, they may also be formed during the incineration, combustion, pyrolysis or other type of thermal processing of BFR-containing waste, by ways rather similar to the chlorinated dioxins/furans. Especially the abovementioned PBDEs show a great tendency to form PBDD/Fs. The picture is made more complex by the mixed chlorinated/brominated dioxins, for which 5020 congeners exist. This issue will and should receive a lot of attention still in the years to come.

BFRs do affect thermal processes for waste treatment, but at the typical temperatures at which BFR-containing wastes are thermally treated (typically 500-1000°C) they will be destroyed and converted mainly to HBr and Br₂, although also other species may be formed. Similar to flue gas scrubbing for HCl this can be done as well for HBr, a recyclable by-product. Depending on *e.g.* the amount of sulphur, water and oxygen present, Br₂ may be formed as well which requires an additional flue gas scrubber. In principle any type of process that allows for the thermal treatment of waste may be used for BFR-containing waste streams. For example, also a "newer", less conventional waste (from an incineration point of view) such a sewage sludge from waste-water treatment was found to contain BFRs [63]. The work with the TAMARA facility in Karlsruhe suggests that a few percent of BFR-containing material can be co-fired in a municipal solid waste incinerator, allowing for recovery of the bromine [37].

Two aspects that have not received sufficient attention must still be mentioned at this point:

- HBr is very corrosive in a wet environment. In the scarce literature on this it was reported that while ASTM 316-type steel can resist dry HBr when tested up to 450°C, but that nickel or Hastelloy metal is to be used when the amount of water in the gas is more than 1 ppmv [67],
- Methyl bromide (bromoform, CH₃Br) is listed as an ozone depleting gas [60] which could mean that its emissions may have to be monitored in the future as part of recent EU directives [68]

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List of Abbreviations

5BT	Pentabromo toluene
ABS	Acrylonitrile Butadiene Styrene B2
ACFSE	the Alliance for Consumer Fire Safety in Europe
ASIC	Application Specific Integrated Circuits
BDE	Bromo diphenyl ether (<i>e.g.</i> deca-BDE)
BFB	bubbling fluidized bed
BFRIP	Brominated Flame Retardant Industry Panel
BFRs	Brominated flame retardants
BSEF	Bromine Science and Environmental Forum
CFB	circulating fluidized bed
DeBB	Commercial decabromobiphenyl
DeBDE	Commercial decabromodiphenyl ether
E+E	Electrical and electronic
EBFRIP	European Flame Retardant Industry Panel
EBTBP	Ethylene bis(tetrabromophthalimide)
ED-XRF	Energy dispersive X-ray fluorescence
EPS	Expanded polystyrene
FR	Flame retardant
FT-IR	Fourier Transform Infrared, Infrared spectroscopy
HBCD	Hexabromo cyclododecane
HDPE	High density polyethylene
HIPS	High Impact Polystyrene
HRGC/MS	High resolution gas chromatography + mass spectrometry
IGBT	Insulated Gate Bipolar Transistor
Masterbatches	Color concentrates and available in the form of granules
MS	mass spectrometry
MSW	Municipal Solid Waste
OcBDE	Commercial octabromo diphenyl ether
PA	Polyamide
PBBs	Polybrominated biphenyls
PBDD/Fs	polybrominated dibenzo -p- dioxins and – furans
PBDEs	Polybrominated diphenyl ethers
PBT	Polybutylene terephthalate
PC	Polycarbonate
PCB	Polychlorinated Biphenyls or Printed Circuit Board
PDBS	Polydibromo styrene
PE	Polyethylene
PeBDE	Commercial pentabromodiphenyl ether
PET	Polyethylene terephthalate
PK	Polyketone
PP	Polypropylene
PPE	Polyphenylene ether
PPS	Polyphenylene sulfide
PS	Polystyrene
PTFE	Polytetrafluoroethylene
PUR	Polyurethane
PVC	Polyvinyl chloride
py-GC/MS	Pyrolysis gas chromatography with mass spectrometric detection
RDF	refuse derived fuels
TBBPA	Tetrabromo bisphenol A
TBPA	Tetrabromo phthalicacid anhydride
TRIS	Tris(2,3-dibromo propyl) phosphate
TUKES	Turvatekniiikan keskus, Finnish safety authority
UPE	Unsaturated polyester
WEEE	Waste from electrical and electronic equipment
XPS	Extruded polystyrene foam