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## Review

# Brominated flame retardants in the European chemicals policy of REACH—Regulation and determination in materials

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## ABSTRACT

The EU REACH legislation will require the registration of 30,000 currently marketed chemicals, including the main commercial BFRs in use (Deca-BDE, HBCD and TBBP-A). Much of the data needed for registration are already available, thanks to risk assessments of continued production and use already undertaken in the EU. Within the authorisation, substitution by less hazardous chemicals is encouraged. Both qualitative and quantitative methods for the analysis of flame-retarded polymers are needed in order that the identity and concentration of the BFRs can be established and compliance with regulations including the RoHS Directive demonstrated. These are reviewed.

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## 1. Introduction

REACH pertains to all chemicals in production within the EU above a specified production volume and documents their potential risks via registration [1]. REACH aims to streamline and improve

the former legislative framework for chemicals within the European Union. The basic goal of REACH is the protection of human health and the environment from the risks posed by chemicals. Following the implementation of REACH, industry will be responsible for assessing and managing risks posed by the chemicals that they produce and for providing appropriate safety information to their users, according to the slogan “no data–no market”! In parallel, the European Union can take additional measures for highly dangerous substances, where this is judged to be appropriate.

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Around 30,000 currently marketed substances will need to be registered under REACH. As many as 1500 substances of very high concern will be subject to authorisation.

The European Chemicals Agency (ECHA) licenses specific uses only. The authorisation is valid only for a limited time, and substitution by less hazardous chemicals is encouraged. Substances subject to authorisation (Art 57 ff) are those which are classified as carcinogenic, mutagenic or toxic to reproduction (CMR) compounds in categories 1 and 2 according to 67/548/EEC; persistent, bioaccumulative and toxic (PBT) compounds according to Annex XIII; or very persistent according to Annex XIII of REACH [2]. In addition, substances considered to be of an “equivalent level of concern” (e.g. endocrine disrupting chemicals) can be included in the candidate list for authorisation. The priority rating for chemicals is based on either wide dispersive use or high production volumes.

For substances produced or imported in quantities of 1 t or more per year per company, manufacturers and importers need to demonstrate that they have appropriately done so by means of a registration dossier including detailed information on safe handling, which must be submitted to the ECHA. For substances which are produced or imported at volumes >10 t per year and per producer or importer, a Chemical Safety Report (CSR) needs to be submitted, which contains (in most cases) the Chemical Safety Assessment (CSA) of the substance which is similar to the risk assessment process under previous regulation. The CSR must provide information on potential PBT or vPvB (very persistent–very bioaccumulative) behaviour, a human health and environmental hazard assessment completed by risk characterisation. Additionally, all the identified uses will be included in the CSR. Any manufacturer or importer shall apply the appropriate measures to adequately control the risks identified in the chemical safety assessment, and include them in the material safety data sheets. Exposure scenarios for the identified uses should also be communicated in the substances’ safety data sheets.

Since the 1960s, brominated flame retardants (BFRs) have been used in a wide variety of polymer and plastics applications that are in widespread use in modern society. These compounds play an important role in saving lives in the event of fire by reducing or inhibiting the fire process after initiation and increasing the time during which an escape can be made. Unfortunately, BFR have also proved to have environmental side-effects. Some of these have proved to have properties which cause them to persist and bioaccumulate in the environment, and can also undergo long-range atmospheric transport via the atmosphere.

Pervasive use of these compounds in consumer products has lead to diffuse discharges to the environment and their discovery in all areas of the environment and numerous studies indicating their persistence and bioaccumulation [3–9].

Several risk assessments of the continued production and use of some BFRs have been performed, both by the flame retardant manufacturing industry and by government authorities responsible for protection of their populations and the environment. Traditionally, government authorities have focused their research activities on establishing fundamental assessment aspects including occurrence, persistence, toxicology and possible routes of exposure [10]. Risk assessments have been carried out for selected substance classes (e.g. the pentabromodiphenylether (Penta-BDE), octabromodiphenylether (Octa-BDE), and decabromodiphenylether (Deca-BDE) formulations, hexabromocyclododecane (HBCD) and tetrabromobisphenol A (TBBP-A)) or are still under investigation [11–15]. The findings of these risk assessments have, in some instances, contributed to the implementation of legal actions, particularly the restriction of the use of polybrominated biphenyls (PBBs) and polybrominated diphenylethers (PBDEs) in electrical and electronic applications [16,17]. While the recent EU

commissioned risk assessment study indicated that “no further action” concerning restriction of use was required for Deca-BDE (confirmed by the EU competent authorities at a meeting in Lisbon on 11 December, 2007) the continued use of Deca-BDE continues to be a contentious issue globally. As such, the industry remains committed to carrying out the various programmes that are currently in progress following the finalisation of the EU risk assessment ([www.ebfrip.org/publications.html](http://www.ebfrip.org/publications.html); [www.bsef.com](http://www.bsef.com)).

In general, the science and technology of flame-retarding polymeric materials is rapidly developing. New innovative ideas, new flame-retardant systems, and a variety of new products are being steadily introduced. New legislation and standards are strongly influencing directions for the development of the technology. The environmental aspects of the use of the flame retardants themselves, of the flame-retardant products, and of their recycling are of special concern. As such, industry and research institutions are actively pursuing effective alternatives to many BFR compounds which can be manufactured economically and which show a wide range of applicability [18].

What are the implications of the REACH legislation for the BFR industry? In 2006, the BSEF (Bromine Science Environmental Forum) published a statement considering the status of BFRs in connection with REACH [19]. BSEF commented that the main commercial BFRs in use (Deca-BDE, TBBP-A, HBCD) have already been subject to advanced testing within EU risk assessments and that these compounds represent some of the most tested chemicals in use globally. It could be argued, therefore, that the main commercial BFRs evaluation work required under REACH has, in large part, already been carried out and the industry is able to meet REACH’s increased requirements for scientific data [19]. According to BSEF, it is not possible to predict the outcome of future scientific testing under REACH for any substance, including BFRs, and it would be mere speculation to do so.

The aim of this paper is to document thorough considerations of aspects of BFRs in materials as they relate to the EU’s REACH programme. The paper also considers methods of analysis and standards related to BFRs incorporated in materials, which can be considered as evaluation tools not only for REACH implementation but also for other purposes including quality control and market surveillance.

## 2. Retrospective view on regulation and legislation

The current EU system for the marketing of dangerous substances distinguishes between “existing” substances (i.e. substances declared to be on the European market prior to September 1981), and “new” substances (i.e. those introduced after September 1981). According to Directive 67/548/EEC, “new” substances have to be tested and their risks to human health and the environment assessed before marketing in quantities above 10 kg per year [2]. More in-depth testing focusing on long term and chronic effects has to be provided for higher production volumes.

Council Regulation 793/93 provides the framework for the evaluation and risk control of “existing substances” which account for more than 99% of the total volume of all substances currently marketed within the EU [20]. Approximately 140 of the “existing” substances were identified as priority substances between 1993 and 2004 and should have been subject to comprehensive risk assessment to be carried out by Member State authorities. The risk assessment process has proved to be very slow. Decisions on further testing of substances can only be taken via a lengthy committee procedure after authorities have proven that a substance may present a serious risk. Proving such a risk is, however, difficult without test results. Final risk assessments have therefore only

been completed for 27 substances to date. Twelve flame retardant compounds have undergone the risk assessment process, accounting for almost 10% of all chemicals under risk assessment. When the assessment concludes that risk reduction is required, the Member States must agree on a risk reduction strategy which may include restrictions on the use or marketing of the substance of concern (Directive 76/769/EEC) [21].

The EU has completed evaluation of four BFR products (the Penta-, Octa- and Deca-PBDE products and TBBP-A) to date and their risk assessment reports (RAR) are available (<http://ecb.jrc.it/esis>). The risk assessment of HBCD is almost complete and the final report should be published in 2008.

### 2.1. Polybrominated biphenyls (PBBs)

PBBs are restricted by the 4th amendment to the marketing and use Directive 76/769/EEC adopted in 1984 and they cannot be used in textile articles, such as garments, undergarments and linen, intended to come into contact with the skin [22]. Indeed, industry voluntarily ceased production of PBBs in 2000. However, in order to accelerate the current system, 76/769/EEC was repealed and incorporated into the REACH regulations. As such, Penta- and Octa-BDE, as well as PBBs can be found in Annex XVII.

### 2.2. Pentabromodiphenylether (Penta-BDE) and octabromodiphenylether (Octa-BDE)

Based on European risk assessments of the Penta- and Octa-PBDE products, the Directive 2003/11/EC was passed as the 24th amendment of Directive 76/769/EEC for the restriction of marketing and use of certain dangerous substances and preparations [17]. The amendment indicated that Penta- and Octa-BDE compounds shall not be placed on the market or used as a substance or as a constituent of preparations in concentrations greater than 0.1% by mass. Additionally, articles may not be placed on the market if they, or flame-retarded parts thereof, contain these compounds in concentrations higher than 0.1% by mass. It is important to note the 0.1% criterion applies to the total concentration of all existing Penta- and Octa-BDE congeners, respectively. Parliament and Council have decided to exclude from this Directive Deca-BDE in view of the findings of its completed RAR and assessment, as well as its importance for fire safety.

Additionally, since 1 July 2006, PBDEs (other than Deca-BDE) and PBBs are banned in electrical and electronic applications according to the "RoHS" Directive [16]. The RoHS acronym derives from the 2002/95/EC Directive title "restriction of certain hazardous substances in electrical and electronic equipment". As the title states, this European Directive restricts the use of specific hazardous substances in electrical and electronic equipment (E&E). Certain applications, materials and components however can be exempted from the restrictions if their elimination or substitution via design changes or materials and components is technically impracticable, or if the negative environmental, health and/or consumer safety impacts caused by substitution outweigh the environmental, health and/or consumer safety benefits thereof. These exemptions are to be reviewed periodically. As such, Deca-BDE was exempted from the RoHS Directive on 15 October 2005 [23]. However, in the beginning of 2008 the European court of justice ruled, that the European commission has acted illegally when it exempted Deca-BDE from the EU ban and decided that the ban should resume from 1 July.

### 2.3. Decabromodiphenylether (Deca-BDE)

The EU's Competent Group of Member State Experts and Authorities officially closed the extensive 10-year risk assessment for Deca-BDE in 2002 with an addendum in 2004 concluding that no further restrictions in its use were required. According to a January 2007 European Chemicals Bureau report, the Deca-BDE RAR has undergone further amendments that have been agreed at Technical and Competent Authority levels, but which are not yet officially published [24]. The brominated flame retardant industry claims, with some justification, that, unlike its potential alternatives, Deca-BDE has been the subject of an EU RAR with no recommendations for discontinuation of its use. Nevertheless, concerns regarding the presence of this compound in the environment, its potential for debromination to yield less brominated and more mobile and toxic congeners and uncertainties with respect to public health persist. It also undergoes long-range atmospheric transport in association with particulate material. As such, there is a popular perception that continued monitoring and minimization of further emissions of Deca-BDE to the environment is necessary. As a consequence, an independent biomonitoring programme and, in relation to this programme, a neurotoxicity study were initialized by industry in consultation with the authorities [25] [www.bsef.com/regulation/eu\\_risk\\_assessm/](http://www.bsef.com/regulation/eu_risk_assessm/).

One option to address issues related to the environmental occurrence of Deca-BDE and other BFR as well could be the initiation of a voluntary industry environmental monitoring programme. Such a programme could be complementary to voluntary industrial emissions control programmes like the Voluntary Emission Control & Reduction Action Programme (VECAP) established by the brominated flame retardant industry.

The European Commission's Scientific Committee on Health and Environmental Risks (SCHER) adopted an opinion in March 2005 on the environmental risk assessment of Deca-BDE [26]. A large part of the new data used for this update have been produced by industry as a response to earlier versions of the risk assessment report. According to SCHER's opinion, the verification of neurotoxic effects and the possible formation of more toxic and accumulative degradation products warrant special concern. Increasing levels in biota (e.g. peregrine eggs), sewage sludge and soils and sediments remote from known sources indicate a diffuse, widespread emission of this compound. Emissions of Deca-BDE may therefore constitute a serious problem. In the PBT assessment, Deca-BDE was found likely to be very persistent according to the criteria presented in the Technical Guidance Document. SCHER strongly recommended further Deca-BDE risk reduction measures [26].

Despite the European risk assessment for Deca-BDE, some Nordic governments continue to seek a ban on Deca-BDE and other brominated flame retardants which have been reviewed at the EU level. Indeed, Sweden has introduced a total ban on use of Deca-BDE in all products, effective from 1 January 2007.

On 21 March, 2007, the European Commission sent a letter of formal notice to the Swedish Government making clear that the Commission considers this unilateral measure unjustified on the grounds of environmental protection in Sweden, unnecessary and inappropriate. This action is the first stage of formal EU legal infringement proceedings. Subsequently, the European Commission and the Swedish Government have established a dialogue to address the incompatibility of the Swedish measure with European law. Norway will also ban the manufacture, import, export, sale and use of Deca-BDE from 1 April 2008 [27].

Recently, the German Umweltbundesamt (UBA) published a statement considering the benefits, risks of brominated flame retardants and possible alternatives. The UBA commented that the precautionary principle should be applied in any case if

chemicals show environmental persistence and/or bioaccumulative behaviour and any release of Deca-BDE, TBPPA and HBCD into the environment should be avoided. The UBA is calling for putting a speedy end to all uses, since less problematic substitutes are available [28].

As a result of VECAP, a first draft Code of Practice regarding the use of Deca-BDE by the plastic and textiles industries was established in the UK to provide appropriate guidance for correct handling and use of this compound and to manage, minimize and monitor its emissions to yield improved environmental performance [29]. Contrary to some perceptions, Deca-BDE is used by many companies in the plastic and textile industry in Germany. Many small and medium-sized plastics companies, who are not members of VKE, have continued to use Deca-BDE, but many are now committing to VECAP [30].

Furthermore, during the first 3 years, VECAP activities have also been focused on the introduction and implementation in Belgium, France, Italy, Germany and The Netherlands. The programme has also been launched in Canada, North America and Japan. VECAP is also being extended to the high production volume brominated flame retardants HBCD and TBBP-A [30].

In 2006, a report was published by the European Chemicals Bureau (ECB) on “Alternatives to Deca-BDE used in polymeric applications in electrical and electronic equipment” [24]. In this study, the production processes of Deca-BDE were reviewed and, in particular, its Nona-BDE content (~3%) which would lead to the presence of restricted BDE compounds exceeding the 0.1% limit (as set by COM decision 2005/618/EC [31]) in typical materials flame retarded with Deca-BDE. The ECB report explored the availability of alternatives to Deca-BDE in polymeric applications for Electrical and Electronic Equipment (EEE). The report concluded that there are alternatives available on the market, although information gaps still exist in relation to their risk assessments and hazard classifications.

#### 2.4. Tetrabromobisphenol A (TBBP-A)

Although it is produced in much higher volumes than the PBDEs, the number and variation of regulations, legislations and assessments is much lower for the reactive BFR TBBP-A. However, the soon to be finalised draft Environment RAR for TBBP-A expresses concern for water and terrestrial compartments. In the Human Health RAR, no health effects of concern were identified from the primary reactive uses of TBBP-A, such as in the manufacture of epoxy resins used in the production of printed circuit boards [14].

However, regarding the marine risk assessment, SCHER agrees that TBBP-A cannot be considered as a PBT chemical [32]. Based on the results of biodegradation tests, TBBP-A is not readily biodegradable but can undergo primary biodegradation to form several products, including bisphenol-A. Excretion of TBBP-A and metabolites from aquatic organisms and mammals is very rapid. No accumulation in lipid tissues has been observed in toxicokinetic studies with mammals. The EU characterises the risk with conclusions (i) there is a need for further information and/or testing and (ii) there is a need for limiting the risks; risk reduction measures which are already being applied shall be taken into account, mainly due to the potential for bisphenol A to be formed [32].

On 15 January 2008, SCHER adopted its opinion on the environmental part of the TBBP-A Risk Assessment, which was concluded in June 2007. In principle, SCHER agrees with the conclusions presented in the RAR. As a result, the EU approved a Risk Reduction Strategy which addresses this risk through industrial site emissions reduction and therefore does not recommend restrictions on TBBP-A's marketing and use.

The SCHER Opinion recommends conclusion (i) for possible TBBP-A degradation to bisphenol-A. This is already fully reflected

in the RAR conclusions, which emphasized that “no risks are currently identified” for this scenario. The Commission will reference the SCHER Opinion, together with the now closed RAR and the Risk Reduction Strategy (RRS), when publishing its final Recommendation on TBBP-A in the Official Journal. The conclusion of TBBP-A's RAR will enable a smooth transition of TBBP-A through the REACH registration procedure, as the science needed prior to registration of TBBP-A is already completed [32,33].

#### 2.5. Hexabromocyclododecane (HBCD)

Few initiatives are underway to assess the need to regulate the use of HBCD. This is in contrast to the fact that HBCD fulfills the PBT criteria and is included in the PBT list of the European chemical substance information system (ESIS). HBCD shows a high bioaccumulation potential, potential for lactational transfer and effects of life-time exposure which require further information and testing considering developmental toxicity according to the RAR proposal. Studies are underway which could influence this conclusion.

HBCD is mainly used in expanded and extruded Polystyrene (EPS and XPS) for thermal insulation foams, in building and construction. As HBCD is produced in volumes greater than 1000 t, it is considered as a high volume substance under REACH and will have to be registered within 3 years of REACH entering into force.

SCHER agreed with most of the approaches for exposure and effect assessment of HBCD which follow the Technical Guidance Document [34]. SCHER recommended a new risk assessment be prepared after completing the data base. Due to the bioaccumulating properties of HBCD, SCHER criticized the study design used for estimating the NOAEL (no adverse effects level). Reduced reference margin of safety (MOS) values used for risk characterisation of occupational, consumer and indirect exposures were also criticized by SCHER and reconsideration was recommended.

HBCD is also covered by the polystyrene foam joint industry emission control programme Self-Enforced Control of Use to Reduce Emissions (SECURE) for EPS/XPS insulation foams application.

### 3. BFRs in REACH—“existing” and potential “new” candidates for registration

The timing of REACH registration is based on the market volumes of the respective chemicals and, for the time being, classifies them into “existing” and “new” categories depending on whether they were initially produced before or after 1981. In the long term, REACH will abolish the existing or new substance distinctions and will establish a single legislative system for the marketing of chemical substances within Europe.

As such, manufacturers, importers and users need to be aware that chemicals falling within the REACH requirements must be registered before being produced, imported, or placed on the market within the EU.

Most of the chemicals defined as “phase-in” according to REACH are those originally placed on the market in the European Community prior to September 1981. These phase-in chemicals are listed in the European Inventory of Existing Commercial Chemical Substances (EINECS). See <http://ecb.jrc.it/esis/index.php?PGM=ein&DEPUIIS=autre>.

Chemicals produced within the member states, but not placed on the market in the 15 years before REACH comes into force, also have to be registered. Additionally, chemicals produced and placed on the market in the EU which had been defined as polymers in the past, but no longer defined as polymer according to the REACH criteria (notification of the new chemical substances in accordance with

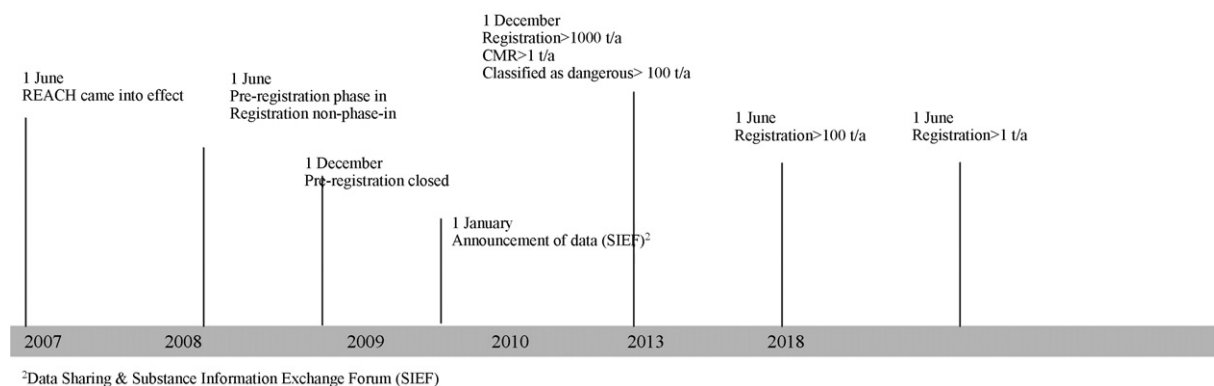


Fig. 1. Timeline for REACH registration deadlines.

Directive 67/548/EEC on the classification, packaging, and labelling of dangerous substances—no longer polymer list) also belong to the phase-in category.

BFRs that can be found in EINECS list are Deca-BDE, HBCD, TBBP-A and bis(pentabromophenyl)ethane (EBP) and therefore these compounds have to be registered.

The global TBBP-A market in 2004 was in the range of 170,000 t, so it is considered to be a high volume chemical under REACH and will be one of the first substances to go through REACH registration (to be completed by December 2010). As it has already been risk assessed, a lot of the required data are already available and can be used for the registration of TBBP-A under REACH.

Similarly, HBCD is currently produced in volumes greater than 1000 t and it is also considered as a high volume chemical and so will have to be registered within 3 years of REACH entering into force. As it is currently being risk assessed, a lot of data are expected to be available for use in the registration of HBCD. No alternative compounds can be used on the main fields of application. The estimated production volume of EBP is >1000 t/a (tonnes per annum) [24].

Though no longer produced in the EU, 7600 t of Deca-BDE are imported each year in addition to 1300 t that are imported in products. In any case, Deca-BDE will have to go through the REACH registration process if placed on the market with a content above 0.1% by mass in products and/or with a market volume above 1 t/a.

Although many large electronic manufacturers claim to have moved to bromine-free alternatives, they have highlighted difficulties in substituting Deca-BDE in high impact polystyrene (HIPS), acrylbutadienestyrene (ABS), and polybutyleneterephthalate (PBTP) applications, citing the lack of good flame retardancy and favourable mechanical properties [24]. In contrast, a Danish EPA assessment concluded that, for all EEE applications, technically acceptable alternatives were available [36].

However, the EINECS was complemented by the European List of Notified Chemical Substances (ELINCS) which is the regulatory scheme for notification of new chemicals in accordance with Commission Decision 85/71/EEC (pursuant to Directive 92/32/EEC, the 7th amendment to Directive 67/548/EEC). For new chemicals, which are not listed on EINECS, the Directive 67/548/EEC requires the submission of a notification dossier prior to marketing. The dossier contains information on the prospective production tonnage of the chemical, as well as its (eco) toxicity and physico-chemical properties. Non-phase-in chemicals already registered according to present regulations are also registered under REACH and should be included in ELINCS. Specific test data are required if defined threshold market volumes are exceeded. Market volume above 100 t/a or 1000 t/a are required to have a testing scheme proposal submitted according to the specifications of arti-

cle 10 of the Regulation 1907/2006/EC. Above 100 t/a information on, e.g. subchronic toxicity (90-day test) and short term toxicity is required whereas additional tests on long-term toxicity (>12 months) and reproductive toxicity are needed for a tonnage band of 1000 t/a.

Fig. 1 shows the timeline for REACH with registration deadlines for the different tonnage bands.

Many large international electronic companies have voluntarily phased out the use of Deca-BDE in their products but have not specified which flame retardants are now being used in its place. A typical replacement scheme may include the use of copolymers with halogen-free organophosphorus compounds for enclosures and other large parts, and the use of alternative BFRs for small parts (<25 g in weight), such as connectors, switches, etc.

The bromine industry has recently developed and is commercialising a new, higher purity, Deca-BDE product (SAYTEX 102 HP) whose Nona-BDE content is not specified.

In the ECB report on Deca-BDE, 27 potential substitutes were identified, of which 16 were halogenated and 11 were non-halogenated. Three of them are also priority substances (TBBP-A, MCCP (medium-chain length chlorinated paraffins), HBCD) which are currently undergoing comprehensive EU risk assessments. Others, including bis(pentabromophenyl)ethane (EBP), resorcinol bis(diphenylphosphate) (RDP), cresyl diphenylphosphate (CDP), triphenyl phosphates (TPP) have also been scrutinized under a national risk assessment programme in the UK [24]. Still, many flame retardant chemicals have not yet been classified because their data set might be incomplete, and/or they have been considered as hazardous or toxic.

The Danish EPA assessed six compounds (ethylene bistetrabromophthalimide (EBTPI), TBBP-A, TBBP-A carbonate oligomer, TPP, red phosphorus and diethylphosphonic acid, aluminium salts) for a range of physical chemical properties, and environmental and human health effects according to a Technical Guidance Document. They concluded that none of the six appear to have more negative impacts on environment, health and/or consumer safety than Deca-BDE [35]. The Danish study on Deca-BDE alternatives adds that two BFRs, namely EBP and EBTPI, have a range of application similar to that of Deca-BDE, and they have been produced and marketed as general purpose alternatives to Deca-BDE by the same companies that produce Deca-BDE. Although more expensive than Deca-BDE, both EBP and EBTPI have superior technical properties (excluding coloration) to Deca-BDE [36]. Now, how will the substitutes be considered by REACH? If they reach similar or higher production volumes, REACH registration will have to be undergone, including risk assessment, etc.

Table 1 shows a list of possible Deca-BDE BFR alternatives [24].

**Table 1**  
Brominated flame retardant alternatives – applications – total production or import volume [24]

Substance name	CAS No.	EINECS	Polymer-type applications	Total production or import volume in EU (in 1000 t-IUCLID <sup>a</sup> )
EBP	84852-53-9	284-366-9	HIPS, ABS, PA, PBTP, PP, PE Minor applications: PC/ABS, HIPS/PPO	No IUCLID sheet EA <sup>b</sup> estimate > 1
EBTPI	32588-76-4	251-118-6	HIPS, ABS, PBTP, PP, PE Minor applications: PC/ABS, HIPS/PPO	EA <sup>b</sup> estimate > 5
TBBP-A epichlorohydrinpolymer	40039-93-8	500-107-7	ABS, PC/ABS	No IUCLID sheet
TBPE	253-692-3	251-118-6	ABS	No IUCLID sheet
HBCD	3194-55-6; 25637-99-4	221-695-9; 247-148-4	HIPS	EU consumption estimated at ~10
TBBP-A	79-94-7	201-236-9	ABS	EU consumption estimated at ~6.5
TBBP-A bis (2,3-dibromopropylether)	21850-44-2	244-617-5	PP	No IUCLID sheet
TBBP-A carbonate oligomer	94334-64-2; 71342-77-3	<sup>c</sup>	PC/ABS, PPO/HIPS, PBTP/PET	No IUCLID sheet
Brominated polystyrene	88497-56-7	<sup>c</sup>	PA, PBTP/PET	No IUCLID sheet
Poly(dibromostyrene)	148993-99-1	<sup>c</sup>	PA, PBTP/PET	No IUCLID sheet
2,4,6-Tris(2,4,6-tribromophenoxy)-1,3,5 triazine	25713-60-4	<sup>c</sup>	HIPS, ABS	Notified substance (confidential)
Brominated epoxy oligomer	68928-70-1	<sup>c</sup>	ABS, PC/ABS, HIPS	No IUCLID sheet

EBP: 1,2-bis(pentabromophenyl)ethane; EBTPI: ethylene bistetrabromophthalimide; TBPE: bis(tribromophenoxy)ethane; TBBP-A: tetrabromobisphenol A; HBCD: hexabromocyclododecane; TBPE: 1,2-bis(tribromophenoxy)ethane. HIPS: high impact polystyrene; ABS: acryl-butadiene-polystyrene copolymer; PA: polyamide; PBTP: polybutyleneterephthalate; PE: polyethylene; PC: polycarbonate; PET: polyethyleneterephthalate; PPO: polyphenyleneoxide; PP: polypropylene.

<sup>a</sup> International Uniform Chemical Information Database (IUCLID) is a software application to capture, store, submit and exchange data on intrinsic and hazard properties on high production volume chemical substances stored according to the format of the OECD.

<sup>b</sup> Environment Agency for England and Wales [24].

<sup>c</sup> Not in EINECS.

#### 4. Overview of polymer analysis methods—pros and cons of the various approaches

##### 4.1. Analyses methods based upon dissolution and precipitation

There are two main applications requiring the analysis of flame retardants in polymeric samples. Firstly, for quality control purposes during the production of electric and electronic equipment in order to certify the absence of PBB, Octa-BDE and Penta-BDE and, thus, compliance with the RoHS Directive. Secondly, in the characterisation of waste polymers in order to qualify them for material recycling or recovery processes.

Most of the investigations considering the analysis of BFRs have been focused on the analysis of BFRs in environmental samples; such as human milk, animal tissues, soils and sediments, air and dust [37–39].

More recently, however, the analysis of plastics for BFRs (e.g. PBBs and PBDEs) has become common as a result of regulation, which has included a number of the states of the USA restricting their use in a broad range of consumer products [16,17].

Environmental samples generally exhibit concentrations at the part per billion level, and sometimes in the part per million range. Due to the complexity of the matrix and the high content of the substances of concern, polymer analysis requires specific treatments to be applied, although the same analytical techniques are applied as for low-level determinations. According to Annex XVII of REACH (former: 24th amendment of 76/769/EC) regulation levels of interest, e.g. for Penta- and Octa-BDE congeners in polymers, are at the high part per million level (1000 ppm or 0.1% by mass). As a result of the RoHS Directive prohibiting the use of PBB and PBDE (at concentrations above 0.1% by mass for PBDE and PBB, respectively, excluding Deca-BDE), manufacturers of EEE have had to inspect large numbers of components that have been purchased from their suppliers in order to demonstrate compliance.

Recycling of polymeric materials has become more and more important in recent years [40]. The recyclability of polymers flame-retardant treated with BFR is potentially hampered due to the possibility of the formation of polybrominated dioxins and furans during the recycling process. As such, identification and sorting of samples according to the flame retardant type and polymer type is necessary prior to recycling.

Formulation additives, including the resin itself, present significant matrix interference challenges in the analysis of BFRs in polymers. Effective removal of these challenges typically requires time-consuming destructive sample pre-treatment (e.g. solvent extraction) steps to gently extract the substances of concern from the matrix while leaving behind as much as possible of the undesirable interfering components. Once pre-treatment has been completed, the extract can be subjected to instrumental analysis by which qualitative and/or quantitative analysis of BFRs can be performed.

Using techniques based upon GC–MS, various types of sample preparation can be applied. One approach is the extraction of the BFR from the polymer by complete dissolution of the polymer in an appropriate solvent. Selecting a solvent capable of dissolving the polymer at room temperature is most desirable, since elevated temperatures may result in thermal stress that can cause BFR degradation. In general, this approach yields good recovery efficiency for the respective BFR, but suitable solvating solvents are not available for all polymer types. Chromatography issues related to system entrapment of the resin and other matrix compounds may also be problematic following a complete polymer dissolution approach. Such entrapment can result in poor chromatographic resolution, hindering the correct detection and identification of compounds and necessitating increased maintenance of the GC–MS system.

Avoidance of interfering or system entrapping compounds by their separation from the sample extract before GC–MS analyses

is highly desirable. Adding a second non-solvent to the extract to precipitate the interfering components (e.g. resin) can be a useful additional step. Ideally, the polymer and other interfering additives (plasticizers, dye stuffs, etc.) are precipitated and the target analytes remain quantitatively in the extract. This method can, however, also generate analyte losses either via target analyte adsorption in the precipitate, or if the solvating behaviour of the target analyte is affected negatively by the non-solvent. Hence, for each type of polymer, a suitable solvent combination needs to be developed. This is rather difficult for unknown materials and makes pre-testing necessary. The same principle has been applied in a patented separation and recycling technique [41]. Analytical methods based on polymer dissolution have been used for the determination of Deca-BDE in HIPS. In this study, the presence of partially brominated PBDE in the Deca-BDE blend was examined. In addition, PBDEs as well as eight PBDF/D congeners included within the German Chemicals Banning Ordinance were monitored after Deca-BDE/Sb<sub>2</sub>O<sub>3</sub> incorporation into the polymer and repeated processing of the same material [42,43]. For the characterisation of an ABS polymer recycling process, an analytical method for selected BFRs has been developed. The dissolution and precipitation behaviour of electronic waste was investigated, followed by instrumental analysis. Hexabromodiphenylether (Hexa-BDE) to Octa-BDE congeners could be identified. The experiments showed that, using dissolution and precipitation steps, the PBDE content of the plastics could be reduced by up to 80% [44]. Imai et al. showed that brominated flame retardant treated plastics that had been reprocessed under well established recycling conditions retain the flame retardant properties of the material [45]. An overview of methods using a dissolution and precipitation step for sample pre-treatment is given in Table 2.

#### 4.2. Analysis methods based upon solid–liquid extraction

For trace analysis, solid–liquid extraction is a commonly applied method. The compounds of interest are isolated using a range of procedures, such as vigorous shaking, ultrasonication, Soxhlet extraction and microwave-assisted or accelerated solvent extraction. Different procedures were examined by Altwaiq et al. to extract high concentrations of BFRs from various materials [48]. These procedures included extraction using supercritical carbon dioxide (sc-CO<sub>2</sub>), solvent-modified sc-CO<sub>2</sub>, solvent extraction and Soxhlet extraction, employing a variety of solvents in order to determine the most effective extraction medium. Extraction with sc-CO<sub>2</sub> yielded low extraction efficiencies (6–20%). The extraction efficiency could be raised by adding toluene, acetonitrile or tetrahydrofuran as a modifier. High extraction efficiencies were achieved for Deca-BDE, TBBP-A and the respective derivatives by using propanol during Soxhlet extraction. The experiments also demonstrated the high extraction capacity of solvents such as toluene, tetrahydrofuran and acetonitrile. The authors recommended the use of toluene or a mixture of toluene and propanol in cases where the extraction efficiency is found to be low.

Silicone and ethylene propylene diene monomer elastomers are frequently used in many industries and are especially common as electrical insulating materials. These, therefore, may represent a significant reservoir of BFRs. Both of these polymers are resistant to chemical analysis, including the analysis of BFRs. Liquid–liquid extraction combined with fluid–solid extraction (Soxhlet extraction) was adopted to measure the content of PBDE in these materials and the extraction efficiency was compared with that of Soxhlet extraction alone. The study showed that the combination of both extraction techniques was more effective for some types of polymer, such as rubber [49].

In general, the analysis of BFR in polymers has been realized using methods based upon either gas or liquid chromatography

[50–52]. GC–MS allows both a high resolution chromatographic separation and a highly specific and sensitive detection. However, the gas chromatographic separation of selected BFR may be hampered due to high boiling points and the possibility of thermal degradation during passage through the heated injection port or the chromatography column (e.g., for Deca-BDE). Furthermore, phenol-based flame retardants require derivatisation before GC analyses can be performed satisfactorily [52]. LC might in some cases represent a suitable alternative to GC techniques. HBCD consisting of three diastereoisomers, can be separated and determined successfully by using LC–MS or LC–MS/MS. These techniques are preferred for environmental analyses, but they can also be used for material analysis. TBBP-A can also be determined using liquid chromatography, thereby avoiding the need for derivatisation prior to analysis. More details concerning recent method developments can be found in literatures [53–56].

In a case study in which PBDEs were determined in a tissue biopsy sample and a blood sample from a young man who showed strong health irritations, components of a TV set were also analysed for PBDE. This was because it has been suggested that there might be a connection between possible PBDE emissions from TV sets and the type of health effects observed. In this study, a method based on Soxhlet extraction followed by GC–MS was applied [57].

Directive 2003/11/EC set a maximum level of 0.1% by mass for Penta- and Octa-BDE congeners in components and products. To verify compliance with this threshold value, a standard measurement method for the determination of selected Penta- and Octa-BDE congeners in polymers based on Soxhlet extraction and GC–MS was developed. This method was also successfully tested in an interlaboratory study conducted according to DIN ISO 5725-2: 2002-12 [58,59]. Reproducibility and repeatability were estimated for determinations in epoxy resin, polyurethane, polystyrene and ABS, and ranged between 0.11–0.25 and 0.03–0.04 mg/g, respectively, relative to a general mean concentration of 1 mg/g. In conjunction with this project another study was carried out, in which the same BFRs and matrices were investigated [60]. Accelerated solvent extraction (ASE), Soxhlet extraction and ultrasonic extraction with various solvent types and system parameters optimised for the best possible performance (e.g. extraction cycles, time, and temperature, influence of polymer type and polymer moisture expansion, etc.) were tested. Soxhlet extraction was found to be the extraction method yielding the most efficient recovery (~80% for PBDE congeners from ABS).

National committee voting on the International Electrotechnical Commission (IEC) “RoHS Test Method” standard (IEC 62321 Ed. 1 Committee Draft for Vote or “CDV”, “Determination of Levels of Six Regulated Substances (lead, mercury, cadmium, hexavalent chromium, polybrominated biphenyls, polybrominated diphenyl ethers)”) closed in December of 2007 [61]. The CDV was unanimously approved with 27 national committees casting approval votes. The approved IEC 62321 CDV contains a test method for the determination of PBB and PBDE in polymers using GC–MS in one of its informative annexes. The IEC method is largely based on and aligned with the “BAM” (Federal Institute for Materials Research and Testing) approach [58].

During the course of the IEC 62321 document development, the IEC working group conducted several international interlaboratory studies (“IIS’s”), including the determination of PBB and PBDE in custom compounded polymer samples (HIPS, ABS and PC/ABS polymer compounds with Penta-BDE, Octa-BDE and Deca-BB) [61,62]. The results were disappointing from both the qualitative and quantitative perspectives, for half of the participating laboratories and for most of the samples. After further revision of the test method, based in part on lessons learned from the second IIS, the working group embarked on a new IIS including samples of PET and

**Table 2**  
Analysis methods for BFR from plastics using a dissolution and precipitation step

Sample material	Extraction	Precipitation step clean-up	Analysis	Reference
HIPS// Deca-BDE	Toluene 1 h extraction Ultrasonic 50 °C	Methanol Filtration Alumina	GC-MS	[42]
HIPS// Deca-BDE	1 h toluene 30 min extraction Ultrasonic 50 °C	Methanol Alumina Filtration	GC-MS	[43]
ABS// Brominated epoxy oligomer, TBBP-A	1.5 h reflux Methylisobutylketone	Hexane Filtration Silica gel Alumina Florisil	GC-MS	[45]
ABS// TBBP-A Hexa-BDE to Deca-BDE	Tetrahydrofuran	Acetonitrile Filtration	GC-MS	[44]
HIPS, ABS// Octa-BDE Deca-BDE	Acetone	Methanol	HPLC-UV (qualitative)	[46]
Different plastic materials// Deca-BDE	Dichloromethane 30 min ultrasonic	Filtration Hexane	IR-spectrum (qualitative)	[47]
Housing and WEEE shredder// PBDE TBBP-A TBPE	Tetrahydrofuran	n-Propanol Filtration	HPLC-UV/MS	[66,67]

Hexa-BDE: hexabromodiphenylether; Octa-BDE: octabromodiphenylether; Deca-BDE: decabromodiphenylether; PBDE: polybrominated diphenylethers; TBBP-A: tetrabromobisphenol A; TBPE: 1,2-bis(tribromophenoxy)ethane; HIPS: high impact polystyrene; ABS: acryl-butadiene-polystyrene copolymer; WEEE: waste of electrical and electronic equipment.

HIPS containing varying known PBB/PBDE amounts and types (including Tetra-BDE, Penta-BDE, Hexa-BDE, Hepta-BDE, Octa-BDE, Nona-BDE, Deca-BDE and Deca-BB. This, the third IIS, was launched and completed in 2007). The third IIS results exhibited considerably better qualitative and quantitative performance than observed in the earlier IIS study.

Thirteen laboratories in Japan took part in an intercalibration study intended to evaluate the accuracy and reliability of the analysis of organobromine compounds, including PBDE, TBBP-A, TBP, and HBCD, in waste TV cabinets. In-house validated methods based on GC-MS or GC-HRMS were used for the determination step. The relative standard deviations for PBDE ranged from 10 to 39% [64].

An alternative technique to *Soxhlet* extraction as presented by Petreas et al. was extraction in a microwave oven [65]. Here, autoshredder and electronic waste were analysed to determine their PBDE content. Investigations of ASE when used for extraction of PBDE and PBB from styrene based polymers have also been published. ASE provided similar results when compared to *Soxhlet* extraction (ASE recovery 70–80% of that obtained using *Soxhlet* extraction) while reducing the solvent consumption by 40% and dramatically reducing the extraction time [66]. ASE used as the extraction step in combination with HPLC-UV-MS has also been described [67].

A fast and simple method for the qualitative identification of BFR using reversed-phase HPLC-UV was developed by Riess and van Eldik [51]. Concentrations of a variety of BFR were determined in TV and personal computer housings collected from a recycling company. The method was developed further for RoHS relevant BFR (PBDE, PBB) and also for phosphorous-based FR with the aim of decreasing the total analytical time. This was achieved using a combination of a phenyl-hexyl-modified HPLC column and ultrasonic solvent extraction [68]. A variety of extraction methods (ASE, *Soxhlet*, microwave) were applied for selected BFRs (TBBP-A, TBPE, Octa-BDE, Deca-BDE, Octa-BB) and various materials (ABS, HIPS). The recoveries ranged between 83–104% for *Soxhlet* extraction and 90–105% for microwave-assisted solvent

extraction. For ASE, a poorer recovery of 60–85% was obtained [46].

A combination of various analytical methods (HPLC, EDX) was tested to see whether they would yield reliable information on the bromine content and structure of the BFRs in electronic components. EDX offers a rapid quantification of the bromine content, while the characterisation of the brominated additives can be achieved using HPLC-UV detection [69].

Recent developments in LC-MS using atmospheric pressure chemical ionisation (APCI) have indicated the applicability of this technique for hydrophobic compounds, including BFR [70].

Schlummer et al. described methods for the determination of FRs in electrical and electronic equipment based on HPLC-UV/APCI-MS and online GPC-HPLC-UV [71,72]. Eleven flame retardants including both those based on bromine and organophosphorus were determined. HPLC-UV/MS was applied to allow the separation, identification and quantification of selected FRs, whereas GPC-HPLC-UV was used as a screening tool. In most cases, negative ion APCI-MS yielded specific mass fragments for the identification of the FRs, except for Penta-BDE and Hexa-BB which did not give rise to sensitive MS responses. As such, the combination of UV and MS seems to be a powerful tool for BFR analytical detection. However, the operation and maintenance of an MS system might be beyond the scope of an EEE producer. Limits of detection for the specified flame retardants obtained for online GPC-HPLC-UV were below 0.05% by mass relative to the dry mass of the polymer. Thus, the method seems to be suitable as a control tool for production or recycling plants of plastics that must demonstrate compliance with current EU regulations.

An overview of the studies described above in addition to further methods using solid-liquid extraction is given in Tables 3 and 4.

#### 4.3. Analysis methods based upon non-destructive methods

Sample pre-treatment followed by gas chromatography-mass spectrometry (GC-MS) is perhaps the most widely used instru-



**Table 3**  
Analysis methods for BFR from plastics based upon solid–liquid-extraction (part I)

Sample material	Extraction	Clean-up	Analysis	Reference
TBBP-A + derivatives TBPE HB Deca-BDE// ABS, PS, ABS/PC, HIPS Television/personal computer housings	(a) Supercritical CO <sub>2</sub> (b) <i>n</i> -Propanol 2 h at 60 °C (c) <i>n</i> -Propanol or toluene 4 h Soxhlet extraction	Filtration	EDXRF IR HPLC-UV GC-MS	[47,48]
PBDE// Silicone rubber Ethylene propylene diene monomer rubber	3 h toluene Filtration + 24 h toluene Soxhlet extraction	Washing with H <sub>2</sub> SO <sub>4</sub> Silica gel Alumina	GC-MS	[48,49]
TBBP-A + derivatives 2,4,6-Tribromphenol TBPE Tetrabromophthalic anhydride PBDE PBB// EEE waste (styrene based)	Methanol <i>n</i> -Propanol 3 h Soxhlet extraction	0.45 μm syringe filter	HPLC-UV	[50,51]
PBDE PBB// Styrene based polymers	<i>n</i> -Propanol ASE	–	HPLC-UV	[65,66]
TBBP-A + derivatives PBDE PBB TBPE 2,4,6-Tribromphenol// Styrene based polymer PU, PC	<i>n</i> -Propanol ASE Microwave extraction Soxhlet extraction Shaking (55 °C)	–	HPLC-UV	[45,46]
TBBP-A + derivatives 2,4,6-Tribromphenol TBPE PBDE PBB Phosphor-organic FR// EEE waste (styrene based)	<i>iso</i> -Propanol Ultrasonic 5 min	0.2 μm syringe filter	HPLC-UV	[67,68]
TBBP-A + derivatives PBDE PBB HB TBPE// EEE waste (mainly polystyrene)	(a) <i>iso</i> -Octane ASE (b) Dissolving in tetrahydrofuran	0.45 μm syringe filters	(a) HPLC-UV/MS (b) GPC-HPLC-UV	[70,71]
TBBP-A, TBPE, Octa-BDE, Deca-BDE// HIPS, ABS, ABS/PC, PPO/PS	Dissolving in tetrahydrofuran Dried on silica <i>iso</i> -Octane ASE	0.45 μm syringe filters	HPLC-UV/MS GPC-HPLC-UV	[72,73]

Hexa-BDE: hexabromodiphenylether; Octa-BDE: octabromodiphenylether; Deca-BDE: decabromodiphenyl ether; PBDE: polybrominated diphenylethers; TBBP-A: tetra-bromobisphenol A; TBPE: 1,2-bis(tribromophenoxy)ethane; PBB: polybrominated biphenyls; HB: hexabromocyclododecane; FR: flame retardants; EEE: electrical and electronic equipment; ASE: accelerated solvent extraction; HIPS: high impact polystyrene; ABS: acryl-butadiene-polystyrene copolymer; PA: polyamide; PBTP: polybutyleneterephthalate; PE: polyethylene; PC: polycarbonate; PET: polyethyleneterephthalate; PPO: polyphenyleneoxide; PP: polypropylene; PS: polystyrene; PU: polyurethane.

mental analysis technique used to distinguish restricted from non-restricted BFRs and for their quantification. This approach, however, is time consuming, requires destruction of the sample and has a relatively high analysis cost associated with the purchase and maintenance of the GC–MS equipment and the high level of expertise needed to operate it. It follows then that GC–MS testing might logically be implemented to determine whether a restricted BFR is present (and in what amount) only after a simpler “screening” test could first demonstrate the potential presence (or absence) of any BFRs or of bromine itself.

Energy dispersive X-ray fluorescence spectrometry (ED-XRF) is possibly the most commonly used analytical technique for screening of restricted substances, largely because of the significant speed advantage it has over traditional analytical methods and its ability to be used with little or no sample pre-treatment. The more sophisticated wave-length dispersive X-ray (WD-XRF)

units are not as commonly employed, due to the higher cost and expertise of operation associated with this instrument. In its simplest form, XRF analysis can provide both qualitative and semi-quantitative, non-destructive elemental analysis (including bromine) in a start to finish time frame of several minutes. This is in contrast to the many hours typically needed for instrumental techniques requiring destructive sample pre-treatment (e.g. solvent extraction–GC/MS). Many users in the electrical and electronic industry supply chain are employing XRF as a screening tool to reduce the time and cost associated with the evaluation of RoHS compliance.

Standards development organizations (SDOs) including the IEC and ASTM International have recognized the value of XRF as an analytical tool for the detection of substances of concern, including restricted BFRs, by analysing the elements of interest, including bromine. Technical committees related to environmental concerns

**Table 4**  
Analysis methods for BFR from plastics based upon solid–liquid-extraction (part II)

Sample material	Extraction	Clean-up	Analysis	Reference
PBDE TBBP-A TBPE// Housing and WEEE shredder	Toluene or <i>iso</i> -octane ASE	–	HPLC-UV/MS	[66,67]
TBBP-A, Deca-BDE// Electronic components	2 h <i>n</i> -propanol Soxhlet extraction	0.45 µm syringe filter	HPLC-UV	[68,69]
PBDE// TV housing Circuit board	16 h toluene 8 h <i>n</i> -heptane 8 h heptane/acetone Soxhlet extraction	Alumina	GC-MS	[52,53]
PBDE// EEE waste Autoshredder waste	Dichloromethane/acetone (1:1) Microwave extraction	Silica/alumina	GC-ECD	[64,65]
TBBP-A, PBDE, TBPE// ABS, HIPS	<i>iso</i> -Octane or <i>n</i> -propanol Soxhlet extraction vs. thermodesorption	Filtration	GC-MS	[73,74]
PBDE, PBB, TBBP-A Polybrominated benzene and phenols// EEE waste	8 h hexane 8 h hexane/acetone (2:1) Soxhlet extraction	Alumina	GC-MS	[51,52]
PBDE, TBBP-A, PBB// EEE waste	16 h hexane/acetone (2:1) Soxhlet extraction	Alumina	GC-MS	[72,73]
PBDE// PS, ABS, HIPS, PU	Toluene 2 h Soxhlet extraction	–	GC-MS	[53,54]
PBDE// PS, ABS, HIPS, PU	Toluene, cyclohexane, hexane, heptane, propanol, methanol Ultrasonic Soxhlet extraction ASE	Silica	GC-MS	[59,60]
PBDE, TBBP-A, TBP, HBCD// Waste TV cabinet	In-house methods	In-house methods	GC-MS GC-HRMS	[63,64]

Deca-BDE: decabromo diphenyl ether; PBDE: polybrominated diphenylethers; TBBP-A: tetrabromobisphenol A; TBPE: 1,2-bis(tribromophenoxy)ethane; TBP: tribromophenol; PBB: polybrominated biphenyls; HBCD: hexabromocyclododecane; FR: flame retardants; (W)EEE: (waste of) electrical and electronic equipment; ASE: accelerated solvent extraction; HIPS: high impact polystyrene; ABS: acryl-butadiene-polystyrene copolymer; PS: polystyrene; PU: polyurethane.

within both the IEC and ASTM are developing XRF test method standards for this application [61,75].

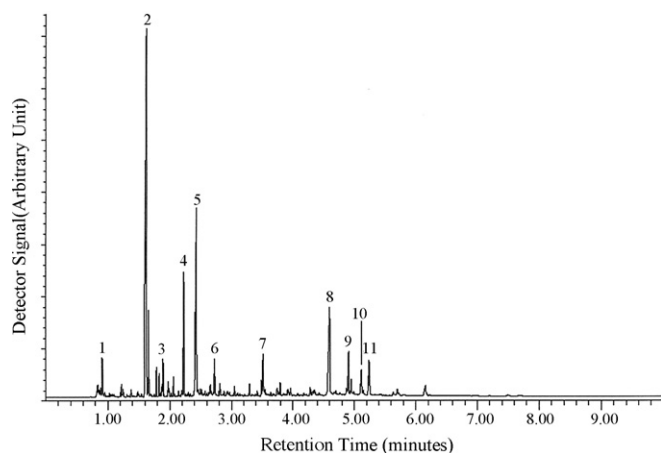
The use of XRF for the detection of halogens including bromine has been reported and plastics standard materials for this analysis are available [77,48]. Assuming that the levels of detection are appropriate, a user may deduce that the absence of elemental bromine detection by XRF in a polymeric material, for instance, is sufficient evidence that a BFR of concern (e.g. PBB or PBDE) is not present. If detected, the user could establish a go/no-go quantity related to the regulation trigger level. Measurements below the trigger level could be deemed to be in compliance. One must keep in mind, however, that appropriate corrections need to be made to relate quantities of elemental bromine detected by XRF to the total amount of potential brominated compound in the sample. A user could implement an XRF screening strategy, for example, to justify the avoidance of more costly and time-consuming sample pre-treatment and GC-MS analysis. On the other hand, if the XRF screening does detect elemental bromine at levels of concern, analysis using sample pre-treatment and GC-MS analysis could be carried out to determine whether restricted BFRs are actually present and at what concentrations.

Like any analytical technique, matrix interferences exist for XRF which need to be accounted for, particularly when used non-destructively. This is especially true for elements whose XRF response is not strong (e.g. cadmium) or if the concentration marking the level of concern is especially low. It is not uncommon for XRF instrument manufacturers to claim elemental detection limits in the low part per million (mg/kg) range for many elements in polymeric matrices, however, these values are, in truth, matrix dependent.

Generally speaking, however, the bromine response for most XRF instruments is quite good and, with the proper understanding of a particular instrument's functioning and capability, suitable for RoHS screening purposes.

While destructive in nature, other test methods for elemental bromine analysis exist which could be similarly employed for polymeric material matrices. Those methods include oxygen flask (*Schoniger* type) or bomb combustion sample pre-treatment with ion chromatography or titration for the determination of bromine content [76,78–80]. The qualitative Beilstein's Test for the detection of halogens can also be useful as a positive screening indicator. Fink et al. reported on the use of total reflection X-ray fluorescence (TXRF) for bromine determination in recycled thermoplastics after dissolution in organic solvents, and the use of laser induced plasma spectroscopy (LIPS) using UV–vis detection as an online characterisation tool without sample pre-treatment for bromine in shredded thermoplastics has also been described [81,82].

The use of infrared analysis as a means of determining whether specific BFRs are present at intentionally added levels can also be considered. Generally, BFRs are used at the 5–20% level by weight in flame-retarded polymer formulations. At this level, the characteristic absorbance bands of specific BFRs can be observed in the spectrum generated by a modern Fourier Transform Infrared (FTIR) spectrophotometer. As with XRF, an FTIR equipped with an attenuated total reflectance (ATR) accessory can analyse samples non-destructively within a few minutes. The spectra of some polymer resins and or their formulation additives can, however, interfere with the absorbance bands of BFRs, making identification difficult at these concentrations. The use of non-destructive FTIR to detect BFRs at contaminant or non-intentionally added levels is not



**Fig. 2.** The pyrogram of a printed circuit board polymer. The tentative identification of major pyrolysates is (1) acetone, (2) phenol, (3) 2-bromophenol, (4) 4-methylethylphenol, (5) 4-methylethenylphenol, (6) 2,6-dibromophenol, (7) 2,6-dibromo-4-methylethenylphenol, (8) bisphenol-A, (9) bromobisphenol-A, (10) dibromobisphenol-A, (11) tribromobisphenol-A. [83].

recommended due to the likely overwhelming spectral responses yielded by the polymer formulation.

At least one report has suggested that Raman spectroscopy is less prone to matrix interference effects than infrared analysis and therefore better suited for rapid non-destructive analysis of BFRs in the acrylonitrile butadiene styrene (ABS) polymer [39]. This study included identification of HBCD, TBBPA and Deca-BDE.

#### 4.4. Analysis methods based upon pyrolysis or thermal desorption of polymers

Quantitative and qualitative analyses of BFRs require the dissolution of the compounds in question in an extractive medium. In contrast to additive BFRs which are mixed into polymer materials, reactive BFRs are copolymerized into the backbone of the polymer, and so are largely inaccessible to extraction. Therefore, the separation, detection and quantification by GC or LC may be difficult to achieve. Pyrolysis–gas chromatography (Py–GC) is one of the techniques that can be used in these circumstances. Py–GC uses thermal energy (pyrolysis) to break down a polymeric chain followed by the separation of pyrolysates with GC with subsequent detection using a mass spectrometer [83].

Luda et al., described the application of Py–GC–MS in the analyses of epoxy resins with incorporated TBBP-A cured using a number of different hardeners. The main volatile products of pyrolysis at 423 °C were phenol, isopropyl- and isopropenylphenol, mono- and di-brominated phenols, bisphenol A, mono-, di-, tri- and tetra-brominated bisphenol-A [84].

The same authors described thermal decomposition at a heating rate of 10 °C min<sup>-1</sup> under nitrogen flow by means of thermogravimetry. Solid residues of decomposed flame-retarded epoxy monomers can be collected at different stages of thermal decomposition in HRTG experiments and analysed by FTIR. To collect high boiling degradation products (HBP), degradation can be carried out in an inert atmosphere. An acetone extract derived in this way can be analysed using GC–MS [85].

Wang et al. investigated printed circuit board applications, in which brominated bisphenol-A has been added along with bisphenol-A to the starting monomers for the epoxy resin. Because of the large number of pyrolysates produced during the pyrolysis of the polymer matrix containing flame retardants, interpretation and identification of all components can be challenging (Fig. 2). The typ-

ical isomer pattern of bromine can be used to identify brominated compounds in the gas chromatogram. Atomic emission detection (AED) can be used as an alternative to MS for the detection of specific-element containing fragments and their relative intensity pattern. Depending on the specific atomic emission lines chosen, AED will detect those components that contain the specific element of interest (such as phosphorus, chlorine, and bromine) [83].

Riess et al. investigated technical flame retardants in polymers originating from electronic waste using an automated Curie-point pyrolysis system. The Curie-point pyrolysis system was directly connected to the split–splitless injector of a GC–MS system. It enables the characterisation of thermoplastic styrene-based polymers containing brominated flame retardant additives, as well as the characterisation of duroplastic polymers with reactive flame retardants embedded in the polymer matrix. TBBP-A, Octa-BB, Octa-BDE and Deca-BDE could be identified in the materials following pyrolysis at 445 °C [77].

A fast and simple method was developed for screening purposes derived from an automobile industry testing method examining the “fogging effect” in a car’s interior [86].

Pieces of PBDE containing polymers were first placed in a conical flask and then in a drying oven at 100 °C for 5 h, which was found to represent the optimum conditions for obtaining the maximum emission efficiency. After sample removal, the conical flask was rinsed with a mixture of hexane and acetone followed by GC–MS analysis [60]. Comparing the method’s sensitivity relative to the maximum levels permitted according to 2003/11/EC for Penta-BDE and Octa-BDE showed that samples containing 0.1% Penta-BDE congeners by mass could be readily detected. The analysis of higher brominated PBDEs seems to be hampered though, due to their low emission behaviour.

## 5. Conclusion

For the main commercial BFRs in current use, registration within REACH may be relatively straightforward. A large amount of the data required for registration has already been generated in response to EU risk assessments. Until REACH is fully implemented, it is unclear whether the promise of improved risk management of chemicals and improved environmental and public health will be realized, although its principles are influencing the approach within the USA as well as in the EU [87].

The determination of BFRs in polymeric materials is needed to demonstrate compliance with regulations included the RoHS Directive, and in e-waste prior to material recycling or recovery processes. Of course, these fields of application require a high throughput of sample analysis due to their broad scope. A broad range of methods are available for the determination of total elemental bromine and concentrations of specific BFR compounds.

The GC–MS technique in combination with appropriate sample preparation or “pre-treatment” prior to analysis seems to be still the method of choice for the determination of BFR compounds. It is both highly selective and sensitive for polybrominated analytes in a variety of matrices and also plastic materials. Both total dissolution and the various solid–liquid-extraction techniques for BFR analyses in polymers have been shown to provide effective recovery efficiency. The United States EPA publication SW-846, entitled Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, is an official compendium of analytical and sampling methods that are globally cited for the analysis of restricted substances (including BFR’s) in electrical and electronic equipment materials. As the SW-846 title suggests however, they are intended for extracting nonvolatile and semivolatile organic compounds from soil and sludge type matrices [88–90].

Thus, analytical methods based on GC–MS are available, although few reference analysis methods standardized according to international protocols (e.g. ISO, IEC) have been published [58,61]. Nevertheless, polymer formulation additives, including the resin itself, can present significant matrix interferences depending on the adequacy and performance of extraction and clean-up methods used. This requires an increased maintenance of the analytical system and makes interpretation of results difficult especially for those levels which are close to requested threshold values. For routine analysis covering an extremely high throughput of samples the operation and maintenance of an MS system might be beyond the scope of producers and material recyclers. Methods based on LC–MS may also be a useful alternative similar to GC–MS, although here too the polymer matrix may lead to a variety of chromatographic problems. The use of LC–MS for this purpose however has not been as widely tested as GC–MS.

Methods based on liquid chromatography in combination with UV detection systems can be implemented as simple and fast techniques, but it is questionable if the specificity and resolution is sufficient for the significant detection and accuracy of discrimination of the components in technical BFR formulations.

The separation, detection and quantification by GC or LC may be difficult to achieve for FR which are copolymerized into the backbone of the polymer. Pyrolysis–gas chromatography (Py–GC) is one of the techniques that can be used in these circumstances. But the large number of pyrolysates produced during the pyrolysis may hamper the interpretation and identification of all compounds. Like the other GC and LC methods, Py–GC is time-consuming, requires significant technical expertise and challenging instrumental maintenance.

Non-destructive methods like XRF provide high throughput capabilities and are useful screening tools to check if bromine is present. However, to confirm whether the source of the detected bromine is restricted BFR compounds requires substance specific analyses techniques (e.g. GC–MS, LC–MS). Furthermore, XRF needs operator expertise to understand potential matrix interference and detection limitations and interpretate results correctly. Low detection limits are required according to the regulation discussed and may not be achieved with EDXRF. Matrix interferences of the various polymer types could also be problem by masking positive findings.

Other spectroscopic methods including Infrared and Raman techniques have been utilized for the detection of BFR compounds. Non-destructive Infrared analysis is best suited for the identification of intentionally added BFRs due to matrix interference. Raman spectroscopy may be less effected by matrix interferences. Neither IR or Raman is well suited for detailed speciation (e.g. congener identification) of BFRs.

One reference material is available since 5 June 2007 consisting of poly(ethyleneterephthalate) granulate that has been fortified with technical mixtures of Penta-, Octa-, Deca-BDE as well as Decabromo biphenyl (IRMM-310). It has been designed to fill the urgent need for reference materials for PBBs and PBDEs in connection with the RoHS regulation, even though it is still not certified ([http://irmm.jrc.ec.europa.eu/html/reference\\_materials\\_catalogue](http://irmm.jrc.ec.europa.eu/html/reference_materials_catalogue)).

All the analysis techniques presented and discussed in this paper can be applied to BFR in polymer materials keeping the various advantages and disadvantages in mind.

The conclusion is that a combination of both, non-destructive for screening followed by trace analysis with the more specific analytical methods is still indispensable for precision and accuracy, also for routine analysis. The broad scope of applications potentially needing the type of BFR analysis' discussed and high throughput requirements however, still pose a challenge to manufacturers and recyclers.

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