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## Assessment of tetrabromobisphenol-A (TBBPA) content in plastic waste recovered from WEEE

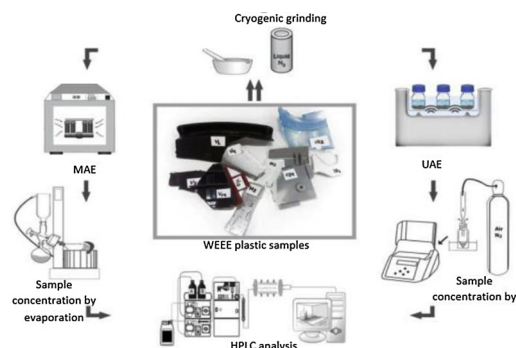
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### GRAPHICAL ABSTRACT



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### ABSTRACT

Due to the variability of additives and polymer types used in electrical and electronic equipment (EEE), and in accordance with the European Directive 2012/19/EU, an implementation of sound management practices is necessary. This work focuses on assessing the content of tetrabromobisphenol-A (TBBPA) in acrylonitrile-butadiene-styrene (ABS), polypropylene (PP), polycarbonate (PC) and their polymer blends (i.e. PC/ABS). A total of 36 plastic housing samples originating from microwave ovens, electric irons, vacuum cleaners and DVD/CD players were subjected to microwave-assisted-extraction (MAE) and/or ultrasound-assisted-extraction (UAE). Maximum mean concentration values of TBBPA measured in DVD/CD players and vacuum cleaners ranged between 754–1146 µg/kg, and varied per polymer type, as follows: 510–2515 µg/kg in ABS and 55–3109 µg/

**Abbreviations:** ABS, acrylonitrile-butadiene-styrene; AC, adapter charger; DL, detection limit; BFRs, brominated flame retardants; CE, circular economy; CFRs, chlorinated flame retardants; CRT, cathode ray tubes; DAD, diode-array detection; DVD/CD, digital video disc/compact disc; EEE, electrical and electronic equipment; EoL, end-of-life; EU, European Union; FRs, flame retardants; GC, gas chromatography; HIPS, high-impact polystyrene; HPLC, high-performance liquid chromatography; IARC, International Agency for Research on Cancer; IP, isopropanol; MAE, microwave-assisted-extraction; MS, mass-spectrometric; LC, liquid chromatography; LCD, liquid-crystal-display; PA, polyamides; PBDD, dibenzodioxins; PBDF, polybrominated diphenyl furan; PBT, polybutylene terephthalate; PC, polycarbonate; PCDD, polychlorinated dibenzo-*p*-dioxin; PCDF, polychlorinated dibenzofuran; PCPW, post-consumer plastic packaging; PCs, personal computers; PDA, photodiode array; PET, polyethylene terephthalate; PMMA, polymethyl methacrylate; PP, polypropylene; PPE, polyphenylene ether; PPO, polyoxymethylene; PP, TD10 polypropylene with talc; PP-MD20, mineral-filled polypropylene; PS, polystyrene; PTFE, Polytetrafluoroethylene; PVC, polyvinyl chloride; PXDD, dibenzo-*p*-dioxins; PXDF, dibenzofurans; sWEEE, small waste electrical & electronic equipment; SoC, substances of concern; TBBPA, tetrabromobisphenol A; TV, television; WEEE, waste electrical & electronic equipment; UAE, ultrasonic-assisted extraction

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kg in PP. The results indicated that MAE was more sufficient than UAE in the extraction of TBBPA from ABS. To optimize the UAE procedure, various solvents were tested. Higher amounts of TBBPA were obtained from ABS and PP using a binary mixture of a polar-non-polar solvent, isopropanol:*n*-hexane (1:1), whereas the sole use of isopropanol exhibited incomplete extraction.

## 1. Introduction

Due to continuous technological advancements, the lifespan of electrical and electronic equipment (EEE) tends to be shorter over the last decades, thus more waste of this type (commonly known in scientific literature as WEEE) is generated. The statistics portal Statista estimated that the global WEEE generation in 2016 was 47.7 Mt (Statista, Global E-Waste - Statistics and Facts, 2018). Given an average annual growth rate of 4 % (Pathak et al., 2017) this could lead to 52.2 Mt in 2021 (Baldé et al., 2017).

To limit any potential environmental impacts associated with such WEEE growth, the European Union (EU) initially established two Directives, 2002/96/EC and 2002/95/EC, along with their most recent recasts (2012/19/EC; 2011/65/EC), where specific limits for various substances of concern (SoC) together with recovery and recycling targets for WEEE, are regulated (European Commission, 2003a, b; European Commission, 2011, 2012). However, the highly ambitious recycling (55–85 %) and recovery (75–85 %) rates set by the EU, can only be achieved if waste fractions (other than metals and glass) are properly managed (Maris et al., 2015).

Plastic represents approximately 20–30 wt% of the total WEEE (Arends et al., 2015; Ma et al., 2016; Schlummer et al., 2007; Taurino et al., 2010). By the end of 2018 more than 10 Mt of post-consumer plastic waste (PCPW) were globally generated, out of a total of 50 Mt of WEEE (Markowski, 2015). Thus, recycling of PCPW from WEEE can substantially aid in meeting the EU recycling targets and consecutively contributing to the circular economy (CE) strategy.

Plastic is a complicated material, containing numerous additives and inorganic fillers (i.e. Cd, Sb, Ti, Sn, Zn, etc.), pigments and flame retardants (FRs) (Arends et al., 2015; Vazquez and Barbosa, 2017; Hahladakis et al., 2018a). Hence, their recycling is a complicated process strongly dependent on the waste stream composition (Maris et al., 2015).

Halogenated FRs are incorporated in the polymers to prevent or reduce their flammability (Vilaplana and Karlsson, 2008). FRs are classified based on their chlorinated (CFRs) or brominated (BFRs) flame retardants content; in the latter case, FRs are considered to be approx. 67 % more effective in terms of thermal stability (Bisschoff, 2000). During mechanical recycling of halogenated plastic, the occurring

thermal stress may lead to the production of corrosive gases, such as HCl or HBr (Wang and Zhang, 2012; Oleszek et al., 2013). As a further complicating matter, in the case of combustion, hydrogen halide gases could be formed as precursors of polyhalogenated dioxins and furans (PCDD/PBDD and PCDF/PBDF), in addition to other organic halogen compounds (e.g. PXDD/PXDF), as well (Taurino et al., 2010; Wang and Zhang, 2012; Barontini et al., 2004; Beccagutti et al., 2016; Schlummer et al., 2006).

Literature data about the presence of BFRs in WEEE plastics, is rather limited (Yu et al., 2017), although these compounds can, potentially, be transferred into the recyclates (Hahladakis et al., 2018a; Samsonok et al., 2015). Consequently, efforts are being made to develop ways for screening the material prior to recycling, in order to remove BFRs from the plastic fraction of WEEE (Paine et al., 2014), as per the 2012/95/EC Directive (European Commission, 2012).

Among the predominant BFRs, the most commonly used compound is tetrabromobisphenol-A (TBBPA) (Covaci et al., 2007; Tollbäck et al., 2006; Tsydenova and Bengtsson, 2011; Pivnenko et al., 2017; Weber and Kuch, 2003), which is covalently bonded into the polymer matrix as a reactive FR (Tollbäck et al., 2006). The primary application of TBBPA is in the production of brominated epoxy resins and polycarbonate (PC) resins (Tollbäck et al., 2006). It can be applied as a FR additive in acrylonitrile-butadiene-styrene (ABS), polystyrene (PS) and thermoplastic polyesters (PET/PBT) (Tollbäck et al., 2006; Luda et al., 2003). Owing to its lipophilic (Ogunbayo and Michelangeli, 2007) and bioaccumulative nature (Vilaplana and Karlsson, 2008; Driffield et al., 2008; Kemmler et al., 2009; Wang et al., 2016), coupled with its wide use, several concerns have arisen about its fate and associated environmental risks, as a result of inappropriate EEE end-of-life (EoL) management processes. Based on *in vivo* experiments, the International Agency for Research on Cancer (IARC) has included TBBPA in group 2A; a carcinogenic potential group (Grosse et al., 2016). TBBPA has been detected in (a) food packaging and household waste plastics (Pivnenko et al., 2017; Driffield et al., 2008), (b) environmental media, such as sludge and sediments (Yu et al., 2017; Brits et al., 2016; de Wit et al., 2010) and (c) biota samples (de Wit et al., 2010; Morris et al., 2004). Thus, further investigation on its presence in waste streams is necessary.

Several studies have examined the composition of waste “e-plastics”

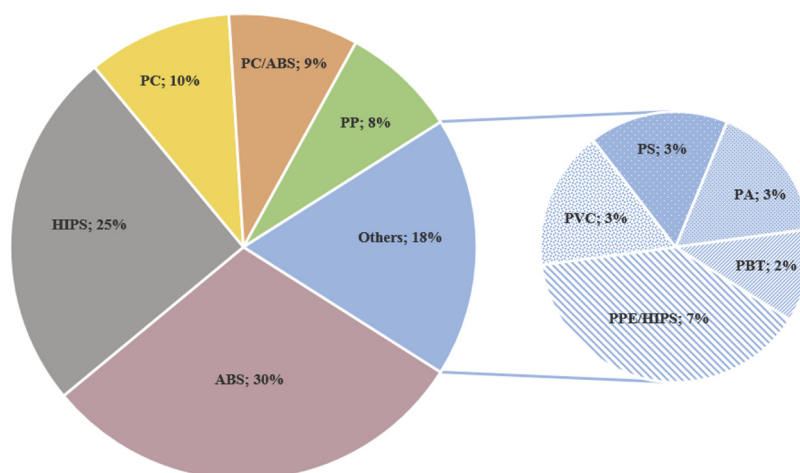


Fig. 1. Typical e-waste plastic composition (adopted by Achilias and Antonakou, (2015)).

**Table 1**  
 TBBPA content levels measured in e-waste polymeric matrices by analytical methods, according to literature.

E-waste type	Polymer type	Number of samples where TBBPA was detected, out of the total number of samples (n)	Extraction method	Solvents used	Analytical method(s) used	TBBPA content (mg/kg)	Reference
Housing polymers (36 monitors & 9 TV sets); Mixed WEEE shredder residues	HIPS; ABS; ABS/PC; PPO/PS	4 (n = 15); 7 (n = 8)	Accelerated solvent extraction	Toluene or isooctane	HPLC-UV/MS	2,700-110,400; 3,100-9,700	(Schlummer et al., 2007)
Mobile phones; PCs; TV sets	PC; ABS; HIPS	1 (n = 3)	Ultrasound assisted extraction	Chloroform/n-hexane	GC/MS	0; 15,804; 0	(Chen et al., 2012)
CRT TV sets; washing machines; PCs (LCD monitors & mainframes); refrigerators;	PP; ABS; PS; HIPS; PC/ABS; PC/ABS + PMMA; ABS + PMMA	15 (n = 19)	Repeated extraction Process	Methanol/water	HPLC-MS/MS	4.64; 0.11; 10.96 & 1.78; 3.01 (mean values)	(Yu et al., 2017)
Large household appliances (cooling & freezing appliances etc.); Small household appliances (toasters, hair dryers, curlers, vacuum cleaners etc.); IT & telecommunications equipment (printers, flat screen monitors CRT monitors etc.); Consumer equipment (CRT screens, CRT TVs etc.)	ABS; ABS/PC; HIPS; PPO; PP	29 (n = 53)	Soxhlet extraction	Cyclohexane/acetone	GC-ECD	30-50; 100-3,700; 60-63,000; 110-4,650	(Wäger et al., 2012)
CRT TV sets (front cabinet; rear cabinet)	Mixed polymers	5 (n = 5)	Ultrasound assisted extraction	Toluene/n-hexane	GC/MS	0.24-67; 0.12-97,000;	(Takigami et al., 2008)
Mixture of consumer products (small appliances; PCs; TVs; fax machines; switches etc.)	PS; ABS; PP; PA; PVC; PC; PET/PBT; PU; PPO; PMMA	-	-	-	-	100-6,000;	(Vehlow et al., 2000)
Small appliances (toasters, vacuum cleaners etc.); IT and communication appliances (PCs, PC monitors, printers, phones, fax-photocopy machines); consumer electronics (TV sets, video recorders, CD players etc.)	Mixed polymers	n = 486	Ultrasound assisted extraction	Toluene	GC/MS (EI) & GC-ECD	1,420 (mean value)	(Morf et al., 2005)
Small appliances (Cat. 2, 3, 4, 6, 7); Small appliances & tools, toys, leisure & sports equipment (Cat. 2, 6, 7); IT & telecommunications equipment & consumer equipment (Cat. 3, 4)	Mixed polymers	10 (n = 11)	Soxhlet extraction	Cyclohexane / acetone	GC-ECD	1,760; 595; 3,675 (average mean values)	(Wäger et al., 2012)
Laptops (plastic-coated wires, ribbon cables and external cables)	Mixed polymers	4 (n = 15)	Soxhlet extraction	Toluene	GC/MS	13.1-242	(Brigden et al., 2007)
LCDs TVs (rear cover; front cover; other PC boards; LCD panel; Power board; PC board for fluorescent; PC board for power supply and fluorescent) & laptop computer (chassis; keyboard top; PC board; cooling fan & speaker; AC adapter; LCD panel)	Mixed polymers	17 (n = 17)	Ultrasound assisted extraction	Toluene	GC/MS	0.015 and 0.068; 0.021 and 0.092; 0.074 and 0.087; 0.0087 and 0.0073; 0.09; 0.89; 2.4 & 2.7; 1.4; 0.8; 9500; 0.081; 0.032	(Kajiwara et al., 2011)
IT & telecommunications equipment (TVs, PCs etc); Small appliances (electric fan, iron, vacuum cleaner, sandwich press etc); Large household appliances (microwave, clothes dryer etc.); Toys, leisure and sports equipment (plastic toys)	-	33 (n = 48)	Ultrasound assisted extraction	Dichloromethane	GC/MS	110-150,000; 26-160,000; 12-110; 150-143,000	(Gallen et al., 2014)

(Chen et al., 2012; Morf et al., 2005; Wäger et al., 2012; Vehlow et al., 2000) and assessed the efficiency of different methods for the extraction and identification of BFRs (Vilaplana and Karlsson, 2008; Paine et al., 2014; Schlummer et al., 2005). Nonetheless, to the authors' best knowledge, inadequate data about TBBPA content was provided; especially for categories: 1 (large household appliances), 2 (small household appliances) and 4 (consumer electronics), also known as small WEEE (sWEEE) (Karagiannidis et al., 2005).

The average plastic content in large household appliances is estimated to be about 17–22 wt%, 48 wt% for small household appliances and approx. 26 wt% for consumer electronics and information and communication technology (ICT) equipment (Delgado et al., 2007). Apart from the various mass fractions of e-plastics existing in the aforementioned three WEEE categories, the polymer types contained in them are dependent on each individual EEE (Chancerel and Rotter, 2009; Martinho et al., 2012); hence, the wide range of polymers present in the WEEE stream, as shown in Fig. 1 (Stenvall et al., 2013; Achilias and Antonakou, 2015). The most abundant type of polymer, typically found in sWEEE, is ABS; however, hi-impact polystyrene (HIPS), PC/ABS blend, polypropylene (PP) and polycarbonate (PC) have, also, been reported (Arends et al., 2015; Delgado et al., 2007).

Although, sWEEE constitute the major share of WEEE (Wäger et al., 2012; Dimitrakakis et al., 2009), most studies have focused on the content of TBBPA in IT equipment (cat. 3), i.e. cathode ray-tube (CRT) TV sets, liquid crystal display (LCD) monitors, and personal computers (Wäger et al., 2012; Kajiwara et al., 2011; Takigami et al., 2008; Brigden et al., 2007) (see Table 1).

The main aim of the present study is to provide a qualitative and quantitative assessment on the content of TBBPA, present in plastics recovered from microwave ovens, electric irons, vacuum cleaners and DVD/CD players. The investigation involved plastics originated from both housing and consumer electronics. For this, a detailed experimental program was followed based on the implementation and comparison of two TBBPA extraction techniques. Finally, the analysis of the TBBPA content was conducted using high-performance liquid chromatography (HPLC) with a diode-array detector (DAD) or mass spectrometry (MS).

## 2. Materials and methods

### 2.1. Collection and preparation of samples

A total of 36 plastic housing samples were obtained from Demontage- und Recycling Zentrum (DRZ), a Recycling, Reuse and Upcycling Company for WEEE located in Vienna, Austria. DRZ operates mainly as a collection point for sWEEE; however, larger units (i.e. washing machines and dishwashers) can also be accepted. WEEE is

**Table 2**

Classification, description and code names of the e-plastic samples collected.

Category of e-waste according to Directive 2012/19/EU	Sample type	Sampling No.	Descriptions
Category 1. Large household appliances	Microwave ovens	M1	ABS
		M2	ABS
		M3	ABS
		M4	ABS
		M5	PP
		M6	ABS
		M7	PC/ABS
		M8	PP-MD20
		M9	PP-MD20
Category 2. Small household appliances	Irons	IR1	PP
		IR2	PC
		IR3	PP
		IR4	PP
		IR5	PP
		IR6	PP
		IR7	PP
	Vacuum cleaners	V1	ABS
		V2	PP
		V3	ABS
		V4	ABS
		V5	PP
		V6	ABS
		V7	PP TD10
		V8	ABS
		V9	ABS
Category 4. Consumer electronics	DVD/CD players	V10	ABS
		V11	ABS
		V12	PP
		V13	ABS
		V14	ABS
		V15	PP
		V16	ABS
CD1	ABS		
CD2	ABS		
CD3	ABS		
CD4	ABS		

manually sorted and disassembled, and the various recovered waste fractions are, in turn, sent to individual partners for material recycling.

E-plastics were randomly sampled, from the 3 aforementioned categories indicated in the Directive 2012/19/EU (European Commission, 2012). More specifically: (i) 9 samples from microwave ovens (included in category 1), (ii) 7 and 16 samples from post-consumers electric irons and vacuum cleaners, respectively (listed in category 2) and (iii) 4 samples from DVD/CD players (category 4) were selected to undergo chemical extraction and analysis for TBBPA content.

The plastic components retrieved from the various devices were

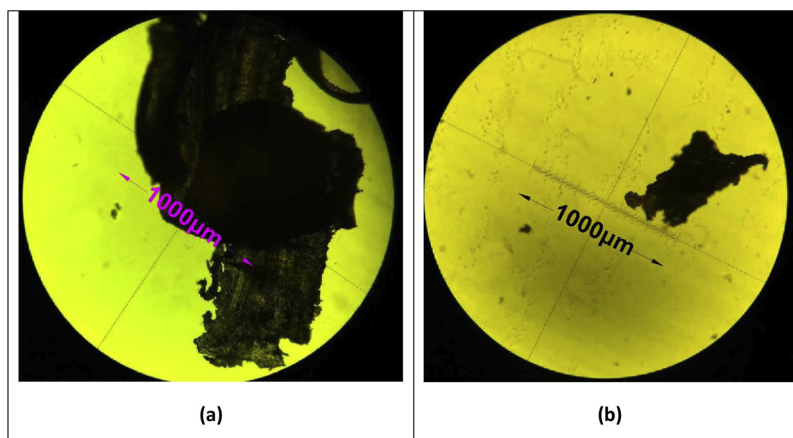


Fig. 2. Photos of plastic particles after (a) manual cutting and (b) liquid nitrogen. Pics were taken using a microscope (plotting scale is shown in  $\mu\text{m}$ ).

manually shredded into foils of less than  $2 \times 1$  mm (Fig. 2a), using hand cutting tools; subsequently, the foils were embattled with liquid nitrogen to further reduce the particle size to less than 1 mm (Fig. 2b), since the cryogenic grinding is more efficient when the surface contact of the sample is small. The samples were, in turn, stored in the dark at a temperature of  $25 \pm 2$  °C to prevent any degradation phenomena (Yousif and Haddad, 2013).

### 2.1.1. Type of polymeric matrices

The characteristics of samples, along with the polymer type and classification of EEE are summarized in Table 2. This information was provided by the manufacturer technical documents on the polymer type and chemical composition of the FRs, indicated in each plastic casing. Based on the EN ISO 11469:2016, which specifies a system of uniform marking for safe handling and proper disposal of this waste stream, all products fabricated from plastic materials are marked.

Within the 3 different waste categories studied, the polymers found were ABS, PP, PC, blends of PC/ABS, blends of PP filled with 10 % talc (PP TD10) and mineral-filled PP granules (PP-MD20), as shown in Table 2. The majority of plastic samples is made from copolymer ABS ( $n = 20$ ) and PP ( $n = 14$ ). In the samples derived from vacuum cleaners, ABS was the dominant polymer type, found in 11 (out of the 16) samples. PP was mainly contained in plastics derived from electric iron devices.

## 2.2. Reagents

TBBPA technical grade, 97 % purity,  $M_r$  543.87 g/mol, CAS number 79-94-7, appropriate for HPLC applications was provided by Aldrich (Stockholm, Sweden). All solvents (*n*-hexane, acetonitrile, isopropanol) used during extraction and analysis of the reference material were HPLC-grade quality and obtained by Sigma-Aldrich, Honeywell and Chem-Lab NV, respectively. Ammonium acetate used for the buffer solution was purchased from Fluka (assay  $\geq 99.0$  %). All used glass containers were rinsed with acetone (Sigma-Aldrich). A working stock solution of TBBPA (10 ppm) was prepared in acetonitrile solution and calibration standard samples from stock solution were dissolved in acetonitrile solution to a concentration of 50 and 2500  $\mu\text{g/L}$ . At the end, in the MAE procedure, a mixture of -commercially purchased- deuterated  $^{13}\text{C}_{12}$ -TBBPA (Wellington laboratories, Guelph, Canada) was introduced in the vial, as an internal standard for spiking the final extracts.

## 2.3. Sample extraction

For the extraction of TBBPA from e-plastics, two techniques were

applied; ultrasonic-assisted extraction (UAE) and microwave-assisted extraction (MAE). A number of samples (7 out of 36) were subjected to both extraction processes in order to compare their efficiency and recommend the optimal one, depending on the polymer type. Particle size (approximately  $1 \times 1$  mm) and solvent media were maintained similar during the efficiency tests of both of the extraction techniques. Different solvent media (polar and polar/non polar mixtures) were examined in relation to the type of polymers (ABS, PP).

Thus, plastic particles were subjected to (i) UAE and (ii) MAE using (a) isopropanol and *n*-hexane (1:1 v/v) and (b) isopropanol, as organic solvents in accordance to relative available literature (Schlummer et al., 2005; Vilaplana et al., 2009; Miyake et al., 2017; Li et al., 2009; Roth et al., 2012). The isopropanol solvent media was used for optimizing only the extraction of TBBPA by ultrasonication. The combinations of solvent system and extraction methods, under various experimental conditions are described in Sections 2.3.1 and 2.3.2.

### 2.3.1. UAE of TBBPA

UAE was performed using an ultrasonic bath (Falc Instruments, 4.5 L bath volume, 40–59 KHz). 1 g of each sample was transferred into a 50 mL glass reagent bottle. In turn, 30 mL of a solvent mixture consisting of isopropanol/*n*-hexane (IP/*n*-hexane, 1:1, v/v) were added as the extractive solution, combining a polar/non- polar solvent. Samples were immersed for a period of 24 h with the bottles submerged halfway into the water of the ultrasonic bath. For achieving the maximum extraction of TBBPA, samples were left under ultrasonic irradiation (40 KHz) thrice for 30 min. By applying the sonication in 30 min intervals any potential degradation of polymers and TBBPA, owing to temperature increase, was avoided. All collected extracts were filtered through a PTFE syringe filter of 25 mm and 0.45  $\mu\text{m}$  pore size (Lab Solutions, Greece). The extracts were then concentrated under a gentle blow of nitrogen, working along with mild heating produced by a controlling dry bath at the bottom (heating reactor). The residue was resolved with acetonitrile to achieve a volume of 5 mL and was placed in amber glass vials to avoid photodegradation of the compound, prior to analysis. The concentration of TBBPA was determined with high-performance liquid chromatographer (HPLC) connected with a diode-array detector (DAD) (HPLC-DAD).

Further UAE experiments were performed using isopropanol as a sole extractive solvent in order to further assess the extraction potential of TBBPA. This time, 30 mL of isopropanol were added, instead of the binary mixture of alcohols and alkanes. At the end of the extraction procedure, the collected extracts were kept at 4 °C until analysed by HPLC-DAD.

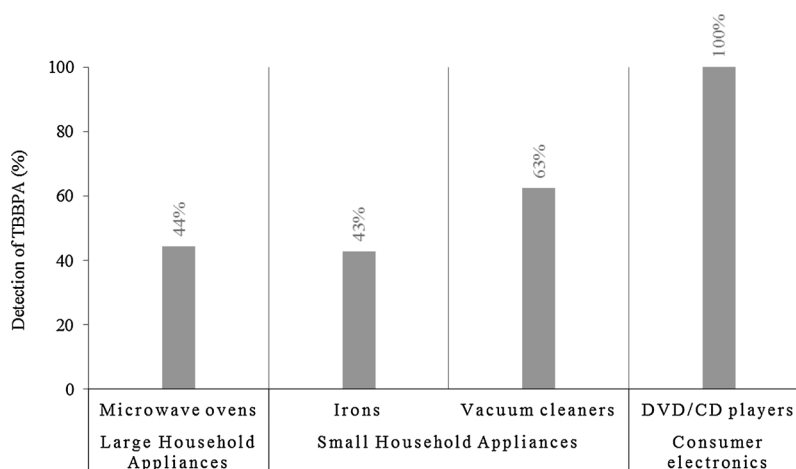


Fig. 3. Detection percentage of TBBPA content in e-plastics samples ( $n = 36$ ). The total number of samples examined differs between devices and categories.

2.3.2. MAE of TBBPA

The MAE procedure followed was in accordance to the one described in (Pivnenko et al., 2017). 1 g of solid sample was directly placed into the microwave designed closed vessels (Multiwave 3000, Anton Paar, Graz, Austria), followed by the addition of 20 mL of extractive solvent, isopropanol/n-hexane (IP/ n-hexane, 1:1, v/v). Microwave heating was set to 100 °C for 60 min, with a gradual cooling at the end. The collected extracts were then subjected to centrifugation at 2500 rpm for 5 min. After decanting the liquid phase, a mixture of deuterated <sup>13</sup>C<sub>12</sub>-TBBPA was introduced in the vial, as an internal standard for spiking the final extracts. In order to reduce the volume to 1.5 mL, a water-bath rotary evaporator (Rotavapor R-205, Büchi, Switzerland) was operated at 40 °C. The collected extracts were filtered using mini uniprep 0.2 µm pore PP filter vials (Whatman, UK) before further analysis with a HPLC/MS (coupled to a tandem mass spectrometer).

2.4. Chemical analyses- instrumental setup

The determination of TBBPA in the samples treated with UAE was performed via the Waters Alliance 2695 HPLC-DAD (Waters 2996 PDA detector). TBBPA was separated in a Luna C18(2) column (5 µm, 4.6 mm × 250 mm) and a security guard column (4 mm × 3 mm), both purchased from Phenomenex, and were thermostatted at 30 °C. The mobile phase was a mixture of ammonium acetate 10 mM, at pH 8 and acetonitrile adjusted with a gradient program. The gradient started with

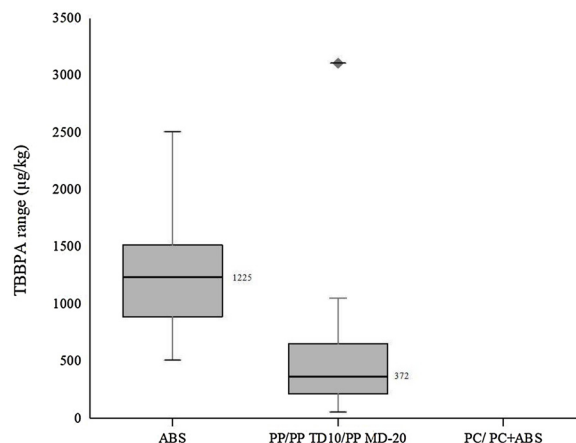


Fig. 5. Mean and range values of TBBPA content in plastic matrices (µg/kg) per polymer type (standard error bars are shown).

80 % acetonitrile, followed by 100 % acetonitrile over a time period of 10 min. The flow rate was 1 mL/min. The injection volume was 100 µL. TBBPA concentration was determined at 210 nm with the PDA detector. Instrument control, data acquisition and evaluation was performed with MassLynx™ software (Waters), whereas quantification was done using a calibration curve, spanning the range of anticipated TBBPA

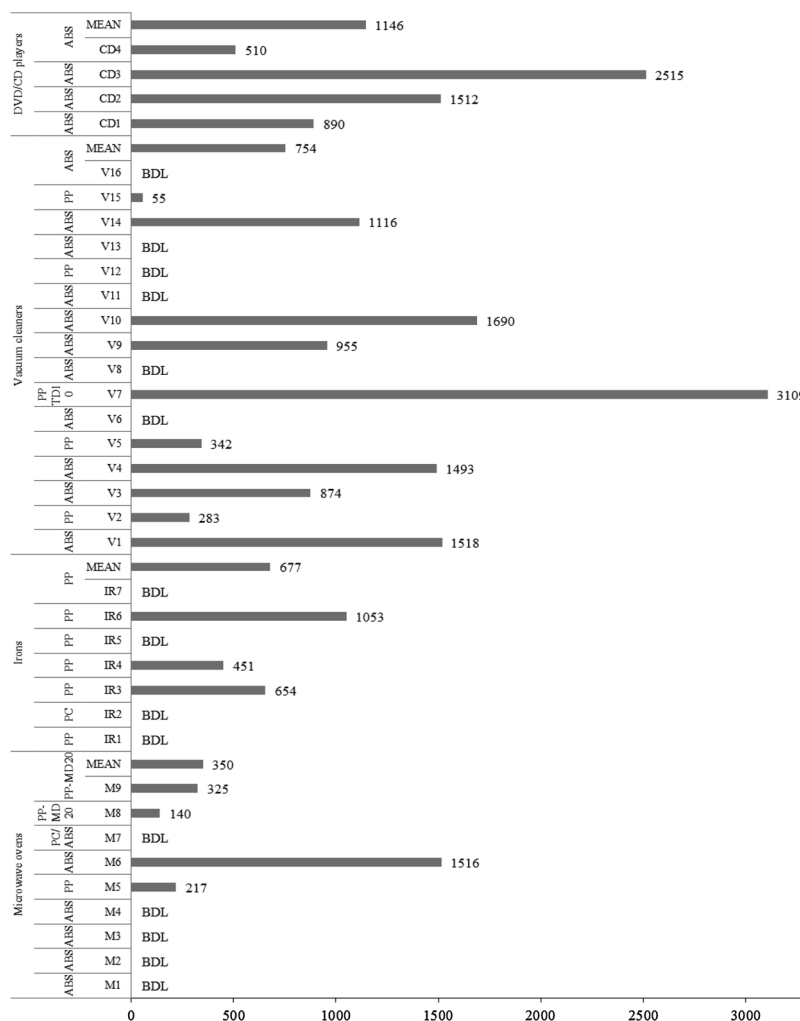


Fig. 4. TBBPA concentration values in e-waste plastics examined (µg/kg). BDL (below detection limit) refers to values that are below the detection limit of the instrument.

concentrations in samples.

A basic calibration with TBBPA was performed in a concentration range of 50 – 2500 µg/L, consisted of 7 calibration points. The detection limit (DL) of TBBPA in the measured samples was 250 ng/g.

Code sample names are presented in Table 2 and correspond to samples that were subjected to chemical extraction and analysis. The results presented in Fig. 3 indicate the presence and frequency of TBBPA in plastics (per category of waste), including microwave ovens, electric irons, vacuum cleaners, and DVD/CD players based on the DL of each analytical method. In turn, Fig. 4 shows the TBBPA concentration in single plastic housings, whereas Fig. 5 illustrates the amount of TBBPA per polymer. The efficiency of UAE and MAE methods is then presented in Fig. 6 in relation to polymer type derived from various units. Finally, optimization of UAE method, associated with the extractive solvent mean, is shown in Fig. 7.

### 3. Results and discussion

#### 3.1. TBBPA content range in household WEEE plastics

Out of a total 36 samples, TBBPA was detected in 21 (ca. 58 % of the plastic casings examined) using HPLC-DAD or HPLC/MS. The target compound was prevalent in the DVD/CD players ( $n = 4$ ) and the vacuum cleaners ( $n = 16$ ) in 100 % and 63 %, respectively (Fig. 3). The results indicated that concentration levels of TBBPA vary significantly even within the same category of waste, ranging from values  $< DL$  to 3109 µg/kg, with a calculated median of 250 µg/kg (Fig. 4).

In particular, mean values of TBBPA detected in plastic housings, per type of WEEE, follow the descending order of: (a) DVD/CD players (1146 µg/kg); (b) vacuum cleaners (754 µg/kg); (c) electric irons (677 µg/kg) and (d) microwave ovens (350 µg/kg). With respect to microwave ovens, TBBPA concentrations ranged from 140 – 1516 µg/kg and were detected in 4 out of 9 samples. For electric irons, TBBPA was found only in 3 samples above DL, ranging from 451 – 1053 µg/kg. In DVD/CD player samples, TBBPA was measured between 510 – 2515 µg/kg. Both the highest and lowest TBBPA content was measured in vacuum cleaners (55 – 3109 µg/kg), in 10 out of 16 samples. Finally electric irons demonstrated a TBBPA content between 451 – 1053 µg/kg. These variations can be attributed to a number of reasons, namely the different composition of e-plastic components, the role of each consumer device, the year of manufacturing and/or the addition of other substitute compounds used also as FRs.

The presence of TBBPA in small household appliances has also been reported in previous studies, in a much wider range (Wäger et al., 2012). It is apparent that the year of the study, the sampling procedure

and the types of polymers examined constitute major factors in the TBBPA content measured, as it is revealed from Table 1.

It has been reported that TBBPA was the most frequently identified BFR tested in 33 out of 48 consumer products (Gallen et al., 2014). In this study, among the examined appliances, CD players exhibited a TBBPA content of 920-153,000 mg/kg ( $n = 3$ ), whereas vacuum cleaners and electric irons demonstrated a much lower content (ca. 26 mg/kg). Both in this, as well as in other studies, TBBPA values were found in higher levels in devices from category 3, compared to large or small household appliances (Schlummer et al., 2007; Wäger et al., 2012; Gallen et al., 2014). Overall, a direct comparison between different works is rather utopic due to the various parameters involved in the sample preparation, extraction method and applied technique. Solvent media and extraction methods may even result in significant differences within the same type of appliances (Table 1). According to literature, for example, TBBPA content in TV sets ranged from 0 to 110,400 mg/kg (Schlummer et al., 2007; Chen et al., 2012; Vehlow et al., 2000).

#### 3.2. TBBPA content range per type of polymer

Fig. 5 presents the TBBPA content per polymer type. Polymers and polymer blends were assigned to one evaluation group per type (ABS, PP/PP TD10/PP MD-20, and PC/PC-ABS). As illustrated in Fig. 5, the range of TBBPA per polymer type varies among the three groups. The higher mean value was found in ABS (1225 µg/kg), followed by PP (372 µg/kg). On the other hand, in polymers made from PC and PC blend with ABS, TBBPA was not detected. This could possibly be attributed to the use of different kinds of FRs contained in the certain polymer type, though uncertainties do exist owing to the limited number of PC samples tested ( $n = 2$ ). Even amongst the same type of polymer, values varied significantly (Fig. 5).

The detection frequency of TBBPA in ABS plastics was considerably lower, as it was detected in 11 out of 20 samples. Comparing the results with other studies, different values were also reported. In one study, for instance, ABS polymers from LCD monitors and PP polymers from washing machines exhibited the highest value of TBBPA. In addition, considering desktop mainframe, TBBPA content in HIPS was found relatively higher than in the one consisted of ABS (Yu et al., 2017).

#### 3.3. Comparison between MAE and UAE efficiency

For the evaluation of the amount of TBBPA extracted, ABS copolymers (V1, V3, V4) and PP polymers (V2, V7, V12, M8) were introduced in both UAE and MAE system, using as solvent media isopropanol/*n*-hexane (IP/*n*-hexane, 1:1, v/v). The results obtained are presented in

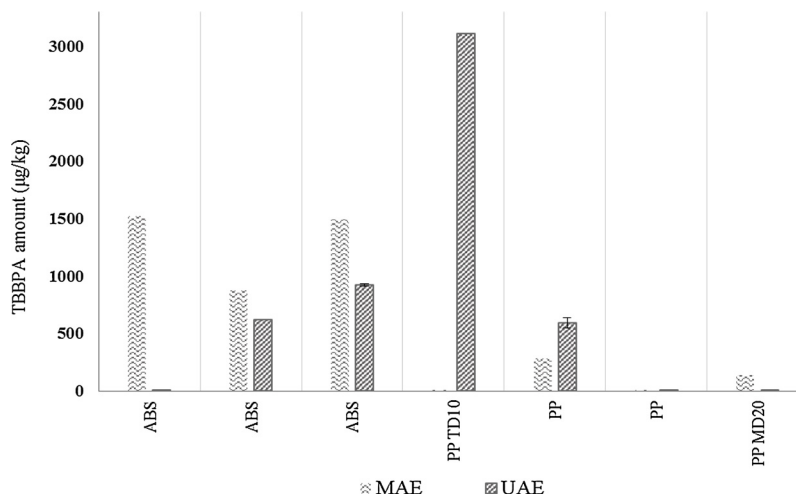


Fig. 6. Amount of TBBPA extracted from ABS copolymers and PP polymers via MAE and UAE method. Error bars represent one standard deviation.

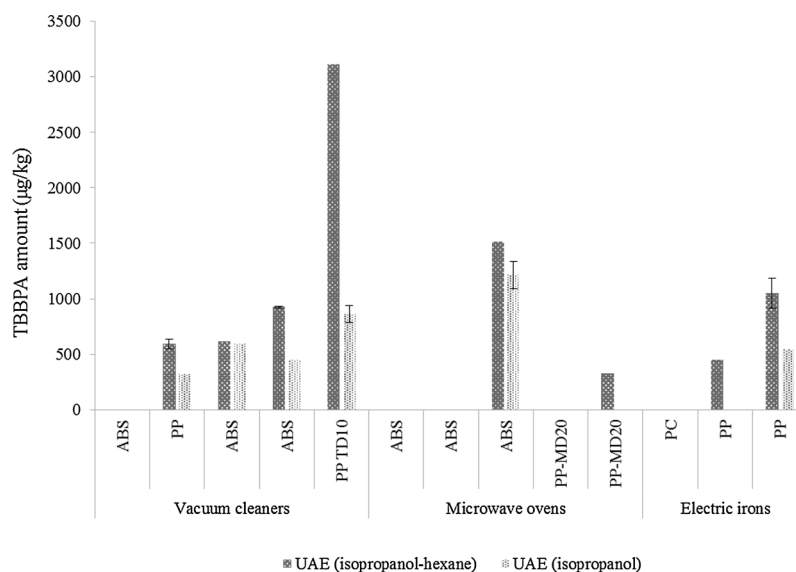


Fig. 7. Dependence of the TBBPA extraction efficiency on the solvent media, isopropanol-hexane and isopropanol, using UAE method. Error bars represent one standard deviation.

Fig. 6.

A significantly higher degree of extraction, under microwave irradiation, was measured regarding samples made from ABS. TBBPA amount levels were detected in approx. 29, 61 or 100 % higher in ABS matrices (namely V3, V4, V1) subjected to microwave irradiation extraction. On the other hand, the TBBPA amount extracted from PP (V2) and PP TD10 (V7) polymeric matrices was found 594 and 3109 µg/kg respectively, while the relative amount was detected 52 and 100 % lower under microwave irradiation. Both methods for V12 (PP polymer) have proved that probably the target compound was not contained in the certain matrix. Referring to sample M8 (PP-MD20 polymer), 140 µg/kg of TBBPA was measured after MAE, in contrast with the < DL amount found with UAE. This difference could be partly attributed to the DL of HPLC-DAD method (250 ng/g) performed upon UAE method.

One of the most crucial steps for determining TBBPA is its chemical extraction from the polymeric matrix. Parameters, such as the nature of the extractive solvents, the operated temperature, as well as time and particle size of the matrices have to be thoroughly considered in order to comprehend how the extraction yield can be influenced in a liquid-solid extraction method (Vilaplana et al., 2009; Bart, 2005; Zhang and Zhang, 2012).

A number of studies have investigated experimental conditions that could enhance the sufficient recovery of TBBPA from polymers using standard polymers as reference material to examine the feasibility of advanced TBBPA extraction and optimise experimental conditions (Vilaplana et al., 2009; Zhang and Zhang, 2012; Altwaiq et al., 2003). Furthermore, various procedures for e-plastic treatment and extraction media have been compared with the scope of extracting the bromine content, in general (Zhang and Zhang, 2012; Altwaiq et al., 2003).

MAE and UAE have been widely used for the recovery of TBBPA from plastic materials (Chen et al., 2012) providing both economic benefits of shorter extraction time, lower reagents consumption (Bart, 2005) and environmental savings in energy consumption (Vandenburg et al., 1998). Hence, previous findings on the optimization of these methods were, also, taken into account in the present study. However, MAE and UAE assisted with isopropanol/*n*-hexane for e-plastics have only been used in HIPS as a standard and ABS as a reference standard/quality control material. Consequently, direct comparison with any literature findings is rather complicated (Vilaplana and Karlsson (2008); Vilaplana et al. (2009) and mostly relies on the evaluation of the findings.

The main question lies on the extent the type of polymer and the extracting solutions/conditions have affected the TBBPA content measured. For instance, in a study where the separation of TBBPA from a HIPS using both MAE and UAE was investigated, the first was found more effective than the latter when a solvent media of isopropanol and hexane was used, exhibiting a difference of approx. 48 % in the extraction yield (Vilaplana and Karlsson, 2008). UAE demonstrated a lower recovery yield mainly due to the limiting temperature adopted in the process. In general, elevated temperatures (60–130 °C), above the glass transition of the polymer, affect the polymeric chain mobility and improve the diffusion rates of the analytes.

In another study, it was highlighted that intermolecular bonds between TBBPA and polymeric matrix could readily break when the extraction is carried out at relatively high temperatures. In the same way, the diffusion rate even in the plastic core or the boundary layer around the polymer surface increases with an increase in temperature. Moreover, the extraction temperature favours the mass transfer of the additives to the solvent media due to the swelling effect of the polymer (Vilaplana et al., 2009).

In accordance to the above findings, determination of BFRs content upon application of the UAE method could be underestimated with regards to the actual amounts of these additives being present in a complex sample matrix. In general, the inadequate disintegration of polymer structure may impede the complete extraction of FRs (Miyake et al., 2017).

The current study compares, also, the extraction efficiencies of UAE and MAE methods for TBBPA extraction in both ABS and PP e-plastics. However, since no reference standards have been used, evaluation of the extraction rates may reflect the accuracy of the findings, taking into account that TBBPA is covalently bounded in polymeric matrices such as a reactive FR, especially in the ABS specimens.

The incorporation of FRs into polymers is also crucial and may influence the feasibility of their identification by impeding or accelerating the extraction and analysis processes. Furthermore, in the current study, the WEEE polymer matrices represented a complex mixture from polymer blends (PC/ABS) or inorganic fillers (for example 10 % talc in PP TD10); so optimization with reference material could further complicate the procedure (Covaci et al. (2009).

Consequently, evaluating the applicability of the two applied methods may contain underestimation or overestimation of the actual TBBPA extracted amounts. Future research is definitely required for obtaining maximum recovery levels of TBBPA in complex matrices,



given the limited number of samples investigated in the present study, and the lack on the effect of particle size and operation temperature.

### 3.4. Effect of extractive solution in UAE system

In order to optimize the extraction efficiency of ultrasonic irradiation, certain samples were treated with different solvent media. The selected samples were marked as ABS ( $n = 6$ ), PC ( $n = 1$ ), PP ( $n = 3$ ), PP TD10 ( $n = 1$ ) and PP-MD20 ( $n = 2$ ). Therefore, as mentioned in Section 2, extractive solutions (a) *n*-hexane and isopropanol (1:1 v/v) and (b) isopropanol were used in the UAE system and the results are illustrated in Fig. 7.

The measured amount of TBBPA, when using only isopropanol as extraction solvent, was found to be significantly decreased. In particular, the recovery of TBBPA from ABS was reduced anywhere between 4–51%. Meanwhile, immersion in isopropanol solution affected, also, the content levels of TBBPA in PP polymers (PP, PP-MD20 and PP-TD10) where a decrease of 46–100% was noticed. Moreover, in 2 out of the 6 PP examined samples, marked as PP and PP-MD20, no extraction of TBBPA was obtained, in contrast to 451  $\mu\text{g}/\text{kg}$  and 325  $\mu\text{g}/\text{kg}$ , obtained respectively, when a mixture of solvents was used after the extraction. As a result, extraction with isopropanol media resulted in an incomplete recovery of TBBPA, especially in PP polymers under UAE method. Lastly, in 3 ABS plastic samples, 1 PP-MD20 and 1 PC type, TBBPA was not detected even when using both solutions.

An additional factor that affects the yield of TBBPA extraction from e-plastics, is the solvent media (Li et al., 2009; Altwaiq et al., 2003). When dissolving a compound, the extraction yield is dependent both on the plastic type, as well as on the polarity of the substance. Thus, the selected solvent system should have a high affinity for both the compounds and the matrices extracted (Vilaplana et al., 2009). Consequently, this means that the solvent could cause swelling effects on the polymer and a selective diffusion of the analytes without disintegrating the matrix (Wang and Zhang, 2012; Vilaplana et al., 2009).

Isopropanol is a polar solvent, and thus the mixture of *n*-hexane/isopropanol is a polar/non-polar solvent medium. The main reason why isopropanol was tested is that as a polar solvent, it may enhance the solubility of TBBPA since the hydroxyl groups tend to make the compound molecule more polar (Xie et al., 2007).

In addition, preliminary studies claimed that alcohols such as methanol, isopropanol and ethanol (Riess and van Eldik, 1998) are capable of dissolving phenols like TBBPA. Any degradation effects on TBBPA solution in isopropanol solvent, when UAE method was applied, didn't occur (Roth et al., 2012). Besides, it has been reported that the use of isopropanol has negligible influence on TBBPA degradation, which in addition, is a phenomenon that occurs in temperatures above 200 °C. In the present study, the temperature was kept under 100 °C, at all times (Marsanich et al., 2004; Qu et al., 2015).

Another important reason for selecting the certain extractive solution is that alcohols are considered less hazardous solvents (Prat et al., 2014). Moreover, isopropanol has already been used as an extractive solution in UAE system (Pöhlein et al., 2005), Soxhlet method (Altwaiq et al., 2003), solvothermal technique (Zhang and Zhang, 2012) and as supercritical fluid (Wang and Zhang, 2012) for the removal of TBBPA from miscellaneous polymer.

Other studies have, also, demonstrated that the use of a mixture of solvent media like isopropanol-*n*-hexane results in higher extraction rates of BFRs, compared to the use of other mixtures of polar-non-polar solvents (methanol-*n*-hexane) (Vilaplana et al., 2009; Vandenburg et al., 1998). Besides, the efficiency of the mixture of solvents could be explained by the acceleration *n*-hexane causes to the diffusion of TBBPA from the polymer structure.

There is a swelling mechanism of polymers that takes place by diffusion of solvent into the microstructure of polymer and can be achieved using non-polar extractive solvents such as *n*-hexane (Bart, 2005). Despite the fact that the performance of UAE was not optimal in

relation to MAE, the solvent mixture of *n*-hexane and isopropanol resulted in the satisfactory recovery of TBBPA compared to the isopropanol solvent media.

## 4. Challenges and perspectives for sustainable management of e-plastics

Due to a documented increase in WEEE any recovery attempt on the plastic fraction embedded in them will boost their recycling and reduce the amount sent to landfills. EC has recently launched a strategy adopting a more 'circular' approach for plastics that comprises the overall impacts (economic, environmental and social) of using recycled e-plastics to support sustainability (European Commission, 2018). Improvements in recycling techniques that turn the waste polymeric parts into new polymer products (Taurino et al., 2010) or allows feedstock recovery for chemicals/monomers/fuels production (Datta and Koczyńska, 2016) could contribute to high-grade products with economic and environmental benefits.

In this way, plastic waste should be considered as a resource. Regarding economics, the potential revenue of 8600 kt from WEEE plastic could reach 12,300 million euros (Kumar et al., 2017). In particular, a cost model calculation showed that the energy for recycling 1 kg of ABS polymer is 71.96 MJ in comparison to the 95 MJ consumed during the production of a virgin ABS polymer (Zhao et al., 2017). Polymer recycling from WEEE provides significant energy savings of about 80 % over virgin material production (Kumar et al., 2017). Thereby, lower energy consumption results in significant reduction of greenhouse gas emissions from mining exploitation. The reduction of CO<sub>2</sub> emissions may be over 2.5 Mt annually from 9.5 Mt of WEEE recycled (EERA, 2017). Lastly, sustainable plastic management can also promote competitiveness and create new economic activities and jobs (Kumar et al., 2017).

Nonetheless, the large number of plastics existing in the WEEE stream, the diversity among product types and the inherent characteristics of plastic, raise specific challenges for their sound waste management. The recycling of WEEE creates additional challenges in complying with EU regulations, such as RoHS and REACH in order to reduce the risk of hazardous emissions and SoC through the recycling chain (European Commission, 2012; Kemmlein et al., 2009). The EU Directive (2012/19/EU) states that plastics containing BFRs should be sorted and managed separately from the non-brominated fraction (European Commission, 2012). This will help mitigate any perpetuate dispersion of contaminants in the recyclates (Hahladakis et al., 2018a; Samsonok et al., 2015; Hahladakis and Iacovidou, 2018). Furthermore, BFRs have been detected in recycled plastic samples indicating that techniques are not properly designed, either for sorting or removing various SoC and additives incorporated in plastic matrices (Hahladakis et al., 2018a, b). Particularly, complete TBBPA removal or degradation may not be achievable during recycling (Pivnenko et al., 2017).

One possible aspect of BFRs remaining in the recycling chain may be the insufficient monitoring of plastics entering the recycling chain due to limitations of the currently implemented technologies (UNEP, 2017).

Sorting of WEEE categories should be considered to avoid unwanted dispersion of SoC in recyclates (Hennebert and Filella, 2018). The heterogeneous polymer mix, present in sWEEE may still remain a practical problem, so a systemic approach should be proposed to determine the occurrence of such chemicals in EoL sWEEE. This should include an accurate marking system for all EEE polymers "put on market", per polymer type and FRs content, especially for complex EEE. Finally, a sound and sustainable recycling process should involve high-quality post-consumer plastics, easily disassembled when embedded in EEE products.

## 5. Conclusions

In this work, the presence of TBBPA was investigated and detected

in discarded microwave ovens, electric irons, vacuum cleaners and DVD/CD players. Its content varied even among plastics of the same category. These variations could possibly be attributed to the different composition of e-plastics and the fire resistance requirements for each individual device.

Furthermore, in the present study both MAE and UAE methods were tested for the extraction of TBBPA. MAE exhibited higher amounts of recovered TBBPA using a solvent media of isopropanol/hexane. This result denotes its superiority over UAE, especially when applied in ABS polymers. A binary mixture of alcohols and alkanes, isopropanol/n-hexane was considered as the most suitable solution for extracting TBBPA from polymeric matrices compared to isopropanol solvent media. Despite the evidences obtained from this study, future research is needed for maximum recovery of TBBPA from complex matrices, via MAE and UAE.

To sum up, investigation on the occurrence of such chemicals in EoL e-plastics may assist to the creation of a database about the content in different types of WEEE in order to enhance the relative plastic fraction separation from the recyclable fraction and contribute to an environmentally-sound recycling process.

### Declaration of Competing Interest

We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

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