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Identification of polymers and flame retardants in sWEEE: personal computers and microwave ovens by FTIR

Master's thesis

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Abstract

During the last decades concern has been raised about the fate of Waste Electrical and Electronic Equipment (WEEE) urging the European Union to take action in order to regulate their management and avoid negative implications related to their improper treatment. Within this context, the WEEE Directive requires the separation of polymers containing some types of Flame Retardants (FRs) before recycling, due to their toxicity. Thus, the development of efficient identification techniques in order to identify the different polymer types and detect FRs is of significant importance in order to comply with the Directive's requirement and increase the quality of recycled plastics. Within the framework of this thesis, experiments were carried out, investigating the performance of Fourier Transform Infrared Spectroscopy (FTIR) in the identification of polymers and FRs found in microwave ovens' and personal computers' plastic housings using two different identification software types, namely the OPUS/SEARCH and the IDENT. After testing the reliability of the FTIR results by other reference identification methods, it was found that the performance of the FTIR technique strongly depends on the identification software and polymer/FR library used. The results of the OPUS/SEARCH software, which were widely validated by the reference analysis, found presence of FRs in the investigated samples at low level, while the most commonly used and significantly toxic FR type, namely the Brominated Flame Retardants (BFRs), was not found at all. On the contrary, the high level of reliability exhibited by this software was not reached by the IDENT software, suggesting that the FTIR can potentially be used as a very useful tool for the investigation of WEEE plastics, primarily for research purposes, contingent upon the appropriate selection of software and libraries.

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Kurzfassung

Das Schicksal von Elektroaltgeräten (EAG) hat sich in den letzten Jahren zu einem vielschichtigen Thema entwickelt und daher hat die Europäische Union Maßnahmen ergriffen, um ihre Behandlung zu regeln. In diesem Zusammenhang fordert die EAG-Richtlinie die Trennung von bestimmten bromierten Flammschutzmitteln vor dem Recycling, damit negative Auswirkungen aufgrund der Toxizität dieser Substanzen vermieden werden. Aus diesem Grund ist die Entwicklung effizienter Identifizierungsmethoden der verschiedenen Polymer- und Flammschutzmitteltypen erforderlich, damit die Richtlinie eingehalten und die Effizienz des Recyclings gesteigert werden kann. Im Rahmen dieser Arbeit wurde ein Experiment durchgeführt, um die Methode Fourier Transform Infrared Spectroscopy (FTIR) hinsichtlich ihrer Leistung bei der Untersuchung von Gehäusekunststoffen von Mikrowellenherden und Computern zu evaluieren. Nach den FTIR Messungen wurden zwei unterschiedliche Softwaretypen (OPUS/SEARCH und IDENT) zur Identifizierung verwendet und die Ergebnisse wurden hinsichtlich ihrer Zuverlässigkeit mittels Referenzmessungen getestet. Die Resultate weisen darauf hin, dass die Leistung der FTIR Methode stark von der benutzten Software und Polymere/Flammhemmer Bibliothek abhängig ist. Die Ergebnisse der OPUS/SEARCH Methode, die einen nur sehr geringen Anteil an Flammschutzmitteln und eine komplette Abwesenheit von bromierten Flammschutzmitteln zeigen, wurden überwiegend von den Referenzmessungen bestätigt. Im Gegensatz dazu hat die IDENT Untersuchung nur ein niedriges Zuverlässigkeitsniveau erreicht. Das bedeutet, dass das FTIR Verfahren ein - hauptsächlich für Forschungszwecke - hohes Potenzial für die Identifizierung von Polymertypen und Flammschutzmitteln aufweist, unter der Bedingung, dass es mit der zweckentsprechenden Software und Bibliothek ausgestattet ist.

Preface

This thesis was conducted within the framework of the master programme "Environment and Bio-Resources Management" of the University of Natural Resources and Life Sciences in Vienna, under the supervision of Professor Stefan Petrus Salhofer. The experimental part of the study was formed, refined and executed at the Institute of Waste Management (ABF-BOKU) of the Department of Water - Atmosphere - Environment. The samples used in the experiments were provided by the dismantling plant Demontage und Recycling Zentrum (DRZ) and were analyzed using the Fourier Transform Infrared Spectroscopy and X-ray Fluorescence Spectroscopy at the laboratory of the ABF-BOKU. Additional reference measurements were collected by means of Near Infrared Spectroscopy and Sliding Spark Spectroscopy at the KERP Center of Excellence Electronic & Environment in Vienna.

Acknowledgements

There are many people who I want to acknowledge for helping me in my studies and in the completion of this thesis. Foremost, among those who helped me academically is my supervisor Professor Stefan Petrus Salhofer, who gave me the opportunity to work with him, and to whom I would like to express my deepest gratitude for his support and guiding throughout both the research and the composing phases of the thesis.

I would also like to especially thank the Director of KERP Center of Excellence Electronic & Environment, Dipl.-Ing. Andreas Schiffleitner, who supported this research by allowing access to the company's facilities, enabling me to collect all the necessary measurements, and my colleagues Giorgia Fanari and Susan Gamarra for their cooperation and their contribution in general.

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List of abbreviations

ABS	Acrylonitrilebutadiene- styrene
ATR	Attenuated Total Reflectance
BFR	Brominated Flame Retardant
CPU	Central Processing Unit
DBDPE	Decabromodiphenylethane
decaBDE	Decabromodiphenyl Ether
EEE	Electrical and Electronic Equipment
EPDM	Ethylene Propylene Diene
FTIR	Fourier Transform Infrared Spectroscopy
FR	Flame Retardant
GC-MS	Gas Chromatography – Mass Spectrometry
HBCD	Hexabromocyclododecane
HFR	Halogenated Flame Retardant
HIPS	High Impact Polystyrene
IR	Infrared
LIBS	Laser Induced Breakdown Spectroscopy
MIR	Mid Infrared Spectroscopy
NIR	Near Infrared Spectroscopy
octaBDE	Octabromodiphenyl Ether
PA	Polyamide
PA6	Polyamide 6
PBB	Polybrominated Biphenyls
PBDD/F	Polybrominated dibenzo-p-dioxins and dibenzofuran
PBDE	Polybrominated Diphenyl Ether
PBT	Polybutylene terephthalate
PC	Polycarbonate
PCs	Personal Computers
pentaBDE	Pentabromodiphenyl Ether
POP	Persistent Organic Pollutant
PP	Polypropylene
PPE	Polyphenylene ether

PPO	Polyphenylene Oxide
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinyl chloride
PXDD/F	Polybromochloro dibenzo-p-dioxin and dibenzofuran
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RoHS	Restriction of the use of certain Hazardous Substances
SB	Styrene-butadiene
SSS	Sliding Spark Spectroscopy
sWEEE	Small Waste Electrical and Electronic Equipment
TBBPA	Tetrabromobisphenol A
WEEE	Waste Electrical and Electronic Equipment
XRF	X-ray Fluorescence Spectroscopy

1. INTRODUCTION

As a result of the significant technological development during the last decades, Electrical and Electronic Equipment (EEE) has become an integral element of human life having a vast range of applications. The continuous development of EEE caused a decrease in prices and, consequently, a decline in its lifespan. Consequently, nowadays, Waste Electrical and Electronic Equipment (WEEE), also known as ‘‘e-waste’’, is one of the fastest growing waste streams. The importance of WEEE stream is not restricted only to its amounts, but also to its content, as it contains a variety of valuable materials, such as metals and plastics, and hazardous substances, such as Brominated Flame Retardants (BFRs). Therefore any lack of proper treatment could cause significant environmental implications and a loss of a significant recycling potential (Cui and Forssberg, 2003; Kolias et al. 2014).

Aiming at regulating the treatment of WEEE and reducing their toxicity, the European Union (EU) has introduced two Directives, the 2002/96/EC and the 2002/95/EC, and their respective recasts. The first is known under the title ‘‘Directive on Waste Electrical and Electronic equipment’’, or “WEEE Directive” and its main aims are the prevention of WEEE and the promotion of WEEE’s recycling (European Commission, 2003a). The WEEE Directive was recently renewed by the 2012/19/EU recast. The 2002/95/EC ‘‘Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment’’, also known as “RoHS Directive”, which came into force on the 1st of July, 2006 and its recast (2011/65/EU), specify maximum concentration limits for six restricted materials, four toxic metals and two BFRs. These maximum concentrations are: 1000 ppm for Polybrominated Biphenyls (PBB), Polybrominated Diphenyl Ethers (PBDE), Lead (Pb), Mercury (Hg) and Hexavalent Chromium (Cr6+) and 100 ppm for Cadmium (Cd). (European Commission, 2003a; European Commission, 2003b; European Commission, 2011; European Commission, 2012).

Considering the restriction of some BFRs by the RoHS Directive and other regulations, in combination with the requirement by the WEEE Directive of removal of plastics containing BFRs from the separately collected WEEE (European Commission, 2012), it is obvious that studies must focus on the identification of FR polymers, in order to remove them from the recyclable fraction and lead to a more efficient and “clean” recycling process. In this context this thesis addresses two issues: the evaluation of different methods for this identification, in order to develop suitable identification techniques to be used in laboratory and industrial scale, and the development of a database, which could indicate which WEEE is more likely to contain Flame Retardants (FRs), in order to ease the separation and generally the recycling process.

1.1 Aim of the thesis

Considering the aforementioned background and the deficiency of knowledge on FR identification, the present thesis, after providing an overview on WEEE plastics and FRs contained in them, aims to evaluate the efficiency of Fourier Transform Infrared Spectroscopy (FTIR) in the identification of polymers and FRs found in different WEEE. Within the framework of this study two important and widely used EEE, the personal computers and the microwave ovens, will be subject of the analysis. Additionally, after the FTIR analysis, it will be inferred whether or not the personal computers and microwaves are likely to contain FRs. As a result this thesis will contribute to an assessment of a methodological approach for identifying FRs in plastics of small WEEE (sWEEE) and determining the product types which are more likely to contain these substances, in order to increase the recycling potential of WEEE and to comply with the regulations.

1.2 Structure of the thesis

This thesis consists of two main parts, the theoretical and the experimental part. The former offers an overview on the theoretical background of the work, while the latter presents the experimental procedure and its results, which are described and discussed in detail. At the end some conclusions are extracted regarding both the theoretical and experimental parts.

The theoretical part (Chapter 2) begins with a short overview on Waste Electrical and Electronic Equipment (WEEE) (Chapter 2.1), focusing on the composition of small Waste Electrical and Electronic Equipment (sWEEE) (Chapter 2.1.1) and more specifically on personal computers and microwave ovens (Chapters 2.1.1.1 and 2.1.1.2). The subject of Chapter 2.2 is plastics used in WEEE manufacture, followed by an overview on Flame Retardants (FR) and their use in WEEE plastics in Chapter 2.3. Chapter 2.4 presents the most important identification methods of polymers and FRs, describing more closely three methods, namely Fourier Transform Infrared Spectroscopy, Near Infrared Spectroscopy and Sliding Spark Spectroscopy, as these are the techniques applied in the experimental part. Finally, the alternatives and challenges of the treatment of WEEE polymers, as well as previous work on the separation of contaminated polymers with FRs are discussed in Chapter 2.5.

Regarding the experimental part (Chapter 3), Chapter 3.1, after an overview on the methodology of the experiment (Chapter 3.1.1), describes the experimental procedure, providing details about the sampling (Chapter 3.1.2), the sample preparation (Chapter 3.1.3) and the sample analysis (Chapter 3.1.4). The results of the analysis are presented and discussed in Chapter 3.2 and, finally, some final conclusions with regard to the present work are listed in Chapter 4.

2. THEORETICAL PART

2.1 Waste Electrical and Electronic Equipment

According to the WEEE Directive, Electrical and Electronic Equipment (EEE) means equipment which is dependent on electric currents or electromagnetic fields in order to work properly and equipment for the generation, transfer and measurement of such currents and fields and designed for use with a voltage rating not exceeding 1000 volts for alternating current and 1500 volts for direct current. Thus, waste originating from EEE, including all components, sub-assemblies and consumables which are part of the product at the time of discarding, is called Waste Electrical and Electronic Equipment (WEEE) or e-waste (European Commission, 2012).

Having a growth rate of 3-5 % annually, almost three times higher than that of average municipal solid waste, e-waste is the fastest growing waste stream in Europe (Gaidajis et al., 2010; Dimitrakakis et al., 2009). During the 1990-1999 period the quantities produced in the EU were approximately 3.3-3.6 kg/resident, while for the 2000-2010 period the quantity was estimated to have raised raised 3.9-4.3 kg/resident (Gaidajis et al.,2010). The global WEEE production is assessed at 20-50 million tonnes per year (Gaidajis et al.,2010; Ongondo et al., 2011), which is equal to 1-3% of the estimated global urban waste production (1636 Mt) (Gaidajis et al.,2010).

WEEE is composed of a variety of materials and several studies have investigated their contribution in the overall WEEE fraction (Achilias and Antonakou, 2015; Freegard et al., 2006; Widmer et al., 2005; Ongondo et al., 2011). The composition of WEEE, as reported by Ongondo et al. (2011), is schematically represented in Figure 1.

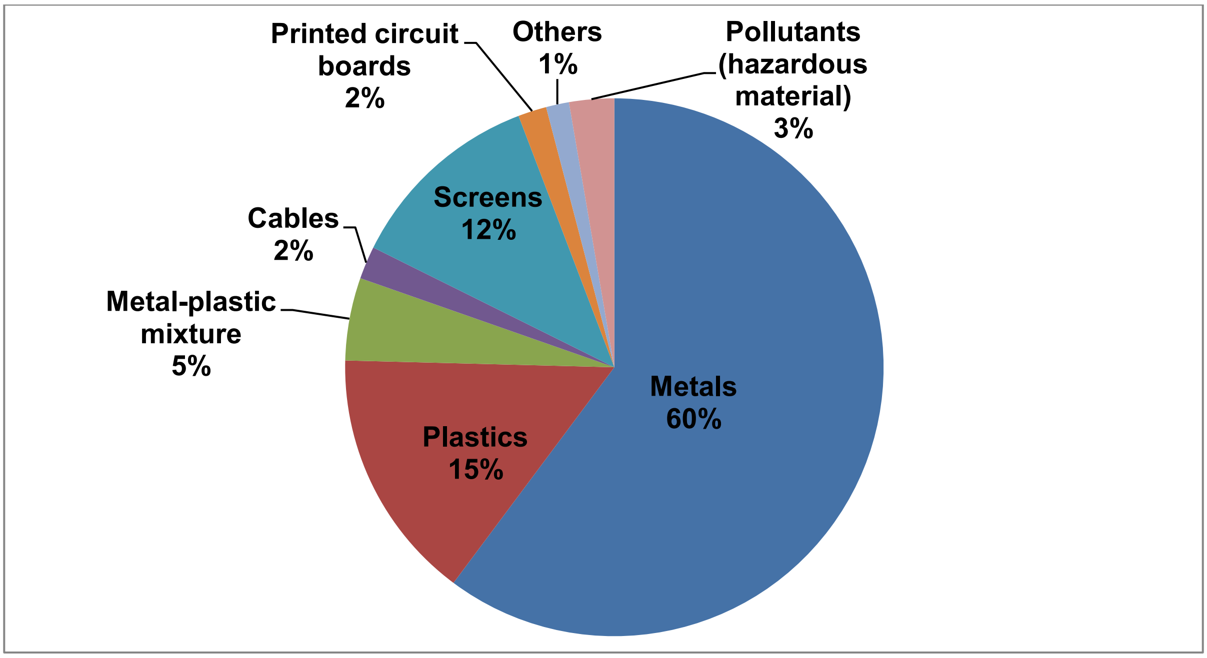


Figure 1: Typical material fractions in WEEE (Ongondo et al., 2011).

According to the study of Widmer et al. (2005), iron and steel are the most dominant materials found in WEEE (by weight), constituting more than half of their total weight, followed by plastics, representing 21 wt.% of WEEE. Non-ferrous metals, including precious metals, constitute 13 wt.% of WEEE, while several pollutants (hazardous materials, see Table 1) and other components represent smaller fractions (Widmer et al., 2005, Ongondo et al., 2011). Considering the composition found in the aforementioned studies, it can be inferred that e-waste include many valuable materials, which can be recycled and recovered, such as plastics, ferrous and other valuable metals, as well as hazardous substances found in various components (e.g. printed circuit boards and screens).

The combination of the increasing quantity and the composition of WEEE led EU to identify them as a priority waste stream and introduced the 2002/96/EC and its recast, 2012/19/EU, in order to regulate the treatment of this kind of waste. Aiming to facilitate the regulation of WEEE management, the WEEE Directive categorized EEE into ten categories (European Commission, 2012). These are:

- Large household appliances
- Small household appliances
- IT and telecommunications equipment
- Consumer equipment and photovoltaic panels
- Lighting equipment
- Electrical and electronic tools (with the exception of large-scale stationary industrial tools)
- Toys, leisure and sports equipment
- Medical devices (with the exception of all implanted and infected products)
- Monitoring and control instruments
- Automatic dispensers

From August 15th, 2018 all EEE will be classified into six categories set out in Annex III of the 2012/19/EU Directive. The new categories will be the following:

- Temperature exchange equipment
- Screens, monitors, and equipment containing screens having a surface greater than 100 cm2
- Lamps
- Large equipment (any external dimension more than 50 cm)
- Small equipment (no external dimension more than 50 cm)
- Small IT and telecommunication equipment (no external dimension more than 50 cm)

As a first priority, the Directive aims to prevent the generation of e-waste. Additionally, it promotes the reuse, recycling and other forms of recovery of WEEE in order to achieve a reduction of the disposal of WEEE. Moreover, it aims to improve the environmental performance of all operators involved in the life cycle of EEE (European Union, 2003b, European Commission, 2012) and to this purpose it establishes the Extended Producer Responsibility (EPR), which requires WEEE producers (manufacturers and importers) to take back their products from consumers and ensure that they are treated using environmentally sound methods (Widmer et al., 2005). Furthermore, the WEEE Directive sets some specific collection goals. Until the end of 2015, each member state was required to achieve a separate collection of household WEEE at an annual rate of at least 4 kg/capita (European Union, 2003b). However, since the beginning of 2016 the collection rate is 45 % of the amount of WEEE generated during the past three years and after 2019 this rate should increase to 65 %.(European Commission, 2012; Ongondo et al., 2011).

2.1.1 Small WEEE

The treatment of sWEEE is relevant, as they are characterized by a high mass percentage in WEEE and because of their high inhomogeneity and complexity. This category contains not only a high number of hazardous and toxic substances, but also a variety of valuable materials. SWEEE are known for their high resource potential, which is mainly connected with the higher proportion of printed circuit boards and contacts especially in IT and telecommunications equipment (Martens, 2011; Grassl, 2013; Salhofer, 2014). Table 1 shows the most important valuable as well as hazardous materials found in sWEEE (Martens, 2011; Grassl, 2013). Another characteristic, which makes the proper management of treatment of sWEEE critical, is the fact that due to their small size, sWEEE are often found in the municipal waste streams (Dimitrakakis et al., 2009).

Table 1: Most important valuable and hazardous materials in sWEEE (Martens, 2011; Grassl, 2013).

Valuable material	Hazardous material
- Steel in housings and functional parts - Copper in motors, transformers, coils, cables and printed circuit boards - Aluminum in chassis and cooling elements - Gold, palladium and silver in contacts, bonding wires and batteries - Tin, lead, silver and bismuth in solders - Zinc, nickel, cobalt and manganese in batteries - Zinc in luminescent layers - Scarce metals (such as tantalum in capacitors; indium in Liquid Crystal Displays (LCDs), mobile telephones, Light Emitting Diodes (LEDs) and thin-film solar cells; ruthenium in hard disk drives and resistors; selenium in copiers) - Rare earth elements in fluorescent lamps (Yttrium, europium) and batteries (lanthanum) - Polymers in housing and other parts - Glass in displays	- Polychlorinated biphenyl (PCB) in capacitors and transformers - PBDE as flame retardant in plastics, printed circuit boards and cables - Mercury in switches, fluorescent tubes, batteries and backlights in LCDs - Lead and cadmium in accumulators and batteries, in display glass and in plastics - Chromium compounds - Others, e.g. asbestos

After the new categorization of WEEE, sWEEE will include a variety of subcategories of the already existing categories. Table 2 shows these subcategories, as well as the share of them in WEEE and typical examples of each subcategory (Huisman et al. 2007; Salhofer and Tesar, 2011). As seen in Table 2, sWEEE constitute almost one third of the total mass of WEEE and include a wide variety of equipment, two of which, the personal computers and the microwave ovens, are investigated within the framework of the study. These two types of equipment were chosen for two reasons:

- They were both considered as priority sWEEE, because they present a high mass percentage in the sWEEE fraction, considering their widespread use and their considerable size compared to other devices included in the sWEEE category.
- Different data concerning the presence of flame retardants exist for these two types of equipment. On the one hand, personal computers have been investigated in several studies regarding flame retardants and most of them proved the presence of these substances in a significant proportion of devices (Aldrian et al., 2015; Chen et al., 2012; Taurino et al., 2010; Reena et al., 2012). Thus, results of other studies could be used in this thesis in order to validate the Fourier Transform Infrared spectroscopy for this purpose. On the other hand, microwaves are reported as less likely to contain flame retardants (French Ministry of Ecology, Sustainable Development and Energy, 2012; Novak, 2001), despite the scarcity of studies exploring the existence of flame retardants. Thus, the experimental part of this thesis aims to provide some data to fill this knowledge gap and prove whether microwaves are indeed free of flame retardants.

Table 2: Composition of sWEEE, share of sub-categories and examples for typical appliances (Huisman et al. 2007; Salhofer and Tesar, 2011).

No.	Subcategory	Typical appliance	Share (mass%)
1C	Large household appliance – small	Microwave oven, electric heating appliance	3.63
2	Small household appliance	Vacuum cleaner, toaster, iron, kettle, electric fan, electric toothbrush	7.01
3A	ICT (excl. CRTs)	Personal computer, keyboard, printer, telephone, laptop	8
4A	Consumer electronics (excl. CRT)	Video recorder, hifi, speaker, radio, remote control, SAT receiver, DVD/CD player	7.82
5A	Lighting equipment	Luminaire	0.7
6	Electrical and electronic tools	Lawn mower, strimmer, pump, garden shear	3.52
7	Toys	Game console	0.11
8	Medical devices	Blood pressure meter	0.12
9	Monitoring and control units	Smoke detector	0.21
Total			31.12

2.1.1.1 Personal Computers

Having applications in several activities, such as work, communication and entertainment, the personal computer is one of the most widespread devices of EEE. As the personal computers' technology is rapidly developing and their prices are decreasing, their lifetime is estimated between 2 and 5 years and approximately 17 million units become obsolete worldwide every year (Kolias et al., 2014; Yamane et al., 2011). A personal computer is made up of several components, such as the monitor, keyboard, mouse, Central Processing Unit (CPU) etc. Within the framework of the present study, the plastic housings of the CPU (also known as tower or computer case) of personal computers were examined. A typical CPU is presented in Figure 2.

According to the WEEE Directive Personal Computers are considered as "IT and telecommunications equipment", however from 15 August 2018, if their external dimensions do not exceed the 50 cm, they will be classified as "small IT and telecommunication equipment". That is the reason why in this study they are considered as sWEEE (European Commission, 2012).

2.1.1.2 Microwave ovens

Another appliance, the usage of which is very widespread in households in Europe is the microwave oven (see Figure 2). It is estimated that the lifetime of a microwave oven has significantly decreased over the last decades and is one of the lowest compared to other household appliances. Their estimated lifespan was found by some studies to be between 4 and 7 years (Dandarian et al., 2012; Gaidajis et al., 2010; Gutierrez et al., 2010). Microwaves are currently categorized as "large household equipment", but from August 15th, 2018 will be considered as "small equipment" (European Commission, 2012).

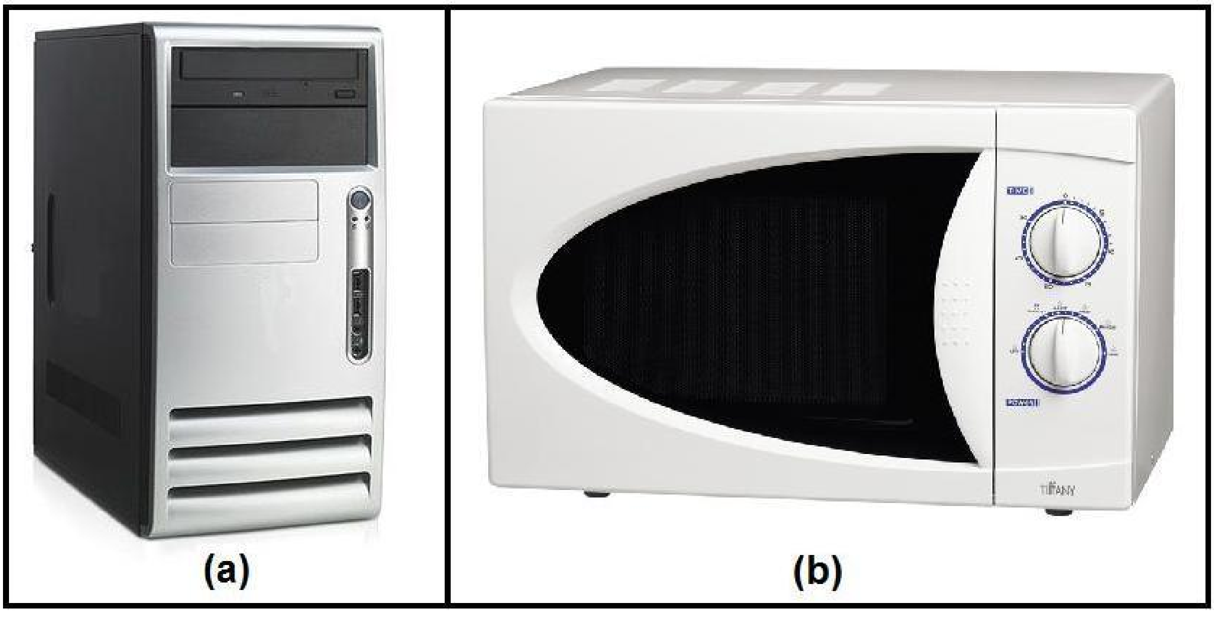


Figure 2: A typical (a) CPU and (b) microwave oven (www.dell.com; www.comparison.com).

2.2 Polymers

2.2.1 Main types of polymers

Polymers in EEE are used in several components, which can be highly visible, such as the housings, or hidden from view, such as cables and printed circuit boards (Kang and Schoenung, 2005). Studies investigating the contribution of different materials in WEEE show a mass fraction of 10-30% for plastics (Achilias and Antonakou, 2015; Martinho et al., 2012; Menad et al., 1998; Ongondo et al., 2011; Taurino et al., 2010; Widmer et al., 2005) with variations in the composition of the polymers (Achilias and Antonakou, 2015). Freegard et al. (2006) report the following composition: Acrylonitrile butadiene styrene (ABS) 30%, high impact polystyrene (HIPS) 25%, polycarbonate (PC) 10%, PC/ABS 9%, polypropylene (PP) 8%, polyphenylene ether (PPE)/HIPS 7%, poly(vinyl chloride) (PVC) 3%, polystyrene (PS) 3%, polyamide (PA) 3%, polybutylene terephthalate (PBT) 2%. A schematic representation is shown in Figure 3.

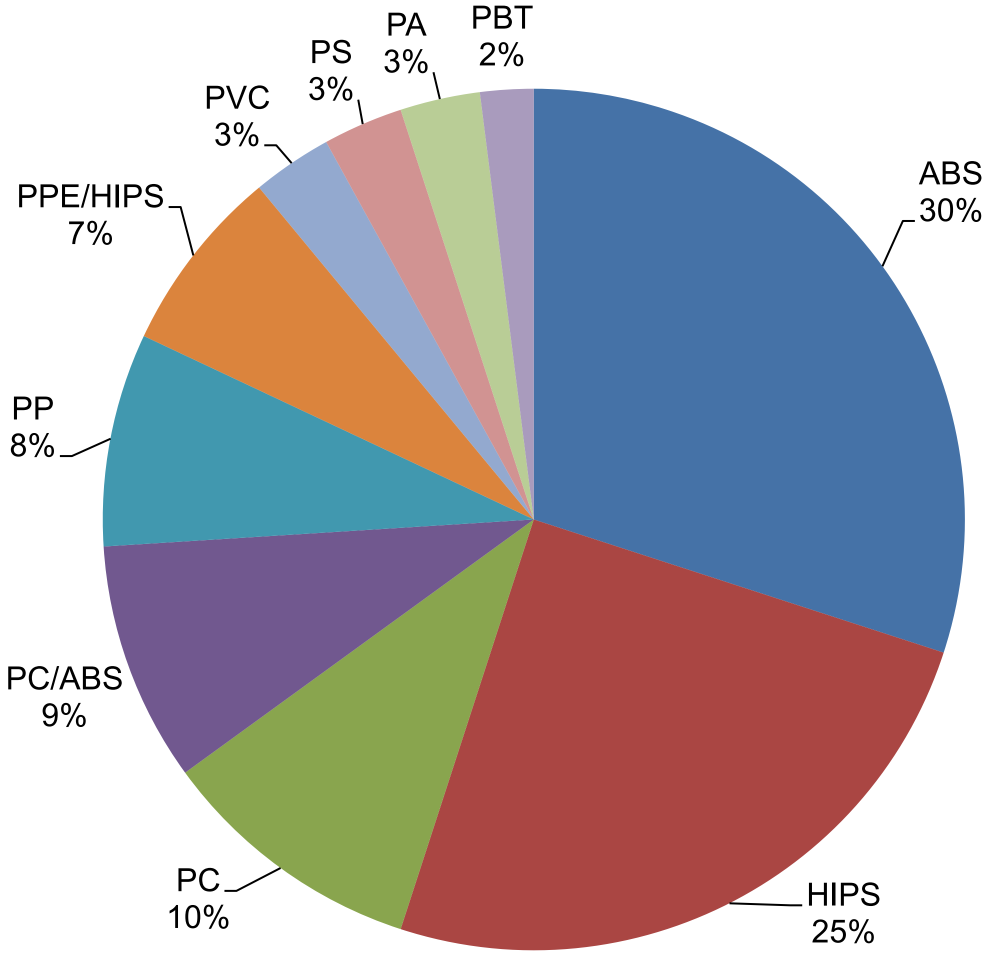


Figure 3: Typical WEEE plastic composition (Freegard et al., 2006).

The most widely used polymers have the following characteristics:

- _ABS:_ It is a terpolymer consisting of three monomers: acrylonitrile, butadiene and styrene. The composition and the properties of ABS can vary depending on the structure of the different phases. Usually, the continuous phase consists of copolymers of styrene and acrylonitrile, while the butadiene consists the dispersed phase (Achilias and Antonakou, 2015). Due to its relatively low cost, ABS is often used for blending with more expensive engineering plastics (Tarantili et al. 2010). Being tough and having high resistance to heat, cold, chemicals and alteration of environmental conditions, ABS polymers have various applications since the 1960s. They are widely used in construction industry, in a variety of household applications, in EEE components, pipes and fittings, as well as automobile interior and exterior trim (Achilias and Antonakou, 2015; Dodbiba and Fujita, 2004).

- _PS_: It is manufactured by the addition polymerization of styrene monomer unit. It has been produced since 1930 and except for the manufacture of WEEE, PS also has several other applications, such as packaging materials, building and construction (Dodbiba and Fujita, 2004).

- _HIPS:_ More widely used in EEE manufacture than PS is HIPS, which is a composite polymer consisting of a PS phase and a dispersed polybutadiene (PB) rubber phase. Polymerization captures the butadiene rubber particles within the polymerizing styrene. The production of HIPS aims at a product with increased impact strength and toughness compared to PS. Beside in EEE it is found in construction and packaging materials, in bottles and in housewares. (Achilias and Antonakou, 2015; Carraher, 2003; Jakab et al., 2003).

- _PC:_ It is one of the most important engineering plastics due to its good optical clarity, excellent mechanical performance, flame resistance, high impact resistance and ductility. Because of these properties, PC is used in many applications including digital media (e.g. CDs, DVDs), automotive industry, glazing in the building and construction industry and food and drink containers. (Achilias and Antonakou 2015; Tarantili et al., 2010). It is often used either individually or as a blend in the manufacture of many different types of EEE (Tarantili et al. 2010).

- _PP:_ This polymer has been produced since the 1950s by the addition polymerization of propylene and it is one of the most versatile polymers. An advantage of PP is its enhanced resistance to water, salt and acid solutions and typical applications include food and drink packaging, medical equipment, automobile battery casings and carpeting markets (Dodbiba and Fujita, 2004).

- _PVC:_ It is produced by polymerization of vinyl chloride monomer (VCM). Combining its low cost with versatility in processing and adequate physical and chemical properties, PVC is one of the most commonly used thermoplastics. It serves a wide variety of applications, such as pipes, window frames, cable insulation, floor coverings, credit cards, etc. (Garcia et al., 2006; Garcia et al., 2007).

2.2.2 Polymers in sWEEE

Polymers make up a high mass percentage of sWEEE and several studies have investigated its extend in the past. Martinho et al. (2012) report a 49.1 wt.% of plastics in sWEEE, while a measurement of the plastic content in WEEE found in the municipal waste stream in Dresden, Germany by Dimitrakakis et al. (2009) showed a percentage of around 34.6 wt.%. Moreover, Chancerel and Rotter (2009) mentioned that in several sWEEE devices have been found polymer contents higher than 50 wt.%.

Martinho et al. (2012) have also investigated the composition of the total plastic fraction in sWEEE in respect to the polymer types they contain. To this purpose they used 1448 devices, including beaters, balances, radios, watches, toasters, facsimiles, printing units, printers, copying equipment and CPUs. The identification was achieved with a Near Infrared (NIR) spectrometer, which could not identify the 14 % of the plastic samples. The results are shown in Figure 4. Twenty one (21) different polymer types were found and the most abundant types in sWEEE are ABS (28% pure ABS and 11% ABS blends), PP (20% pure PP and 6% PP blends) and PS (8% pure PS and 3% PS blends), while Wäger et al. (2009) report that the most dominant types are PP, HIPS and ABS.

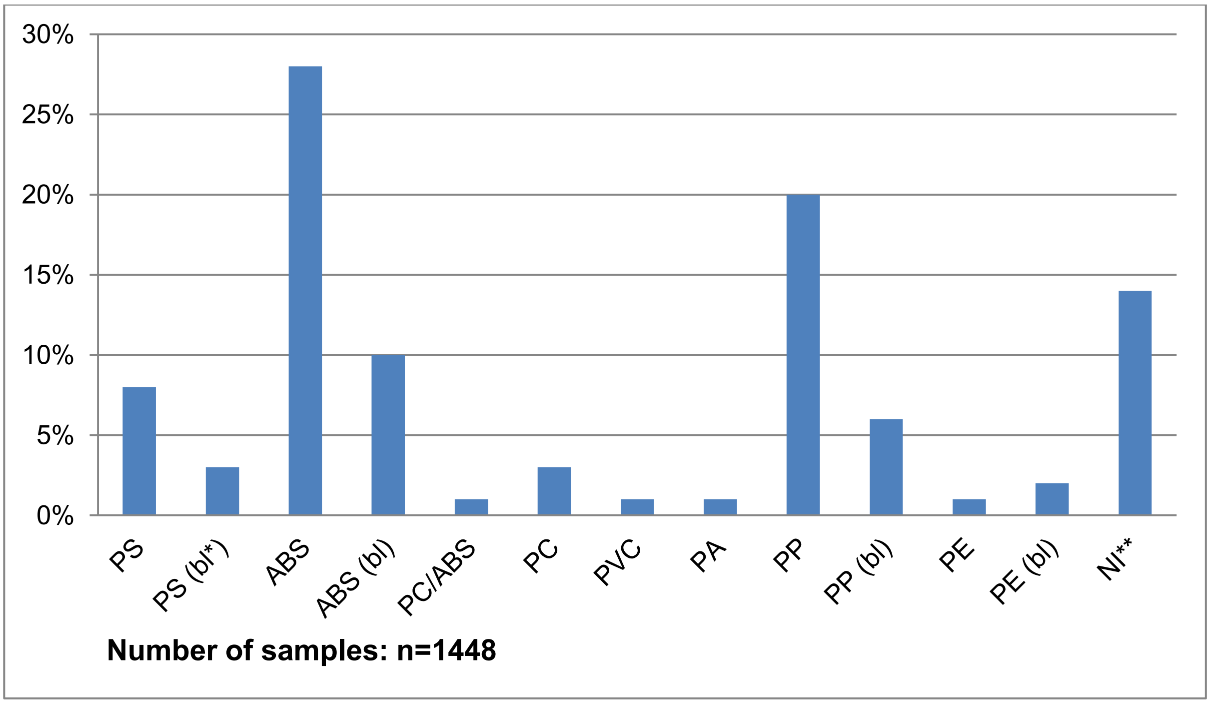


Figure 4: Plastic composition in sWEEE (* bl: Blends, **NI: Not Idenified) (Martinho et al., 2012).

Several studies report the polymer share in personal computers (Kang and Schoenung, 2005; Pedersen, 1996; Martinho et al., 2012; Wäger et al., 2010), as well as the type of polymers used (Reena et al., 2011; Freegard et al., 2006; Wäger et al., 2010). Kang and Schoenung (2005) and Pedersen (1996) report a 23 wt.% of plastics in a complete personal computer, while, regarding CPUs, Martinho et al. (2012) found only 3.5 wt.% of plastics. Wäger et al. (2010) mention that in computers a relatively small number of different plastics is applied. Table 3 presents the percentage of different polymer types used in personal computers, as reported by Reena et al. (2011) and Freegard et al. (2006). The percentages in the work of Freegard et al. (2006) were obtained by interviews from technical staff of the industry of personal computers, who were asked to state the most commonly used type of polymers in their existing product range. The most abundant types according to Reena et al. (2011) are ABS and polyphenylene oxide (PPO), while Freegard et al. (2006) report similar amounts of ABS, but much higher of HIPS and PC/ABS. The results of the study of Freegard et al. (2006) correspond with those of Wäger et al. (2010), who additionally report that polymers such as PVC and PC are of less relevance.

Table 3: Composition plastics in personal computers (Reena et al., 2011; Freegard et al., 2006).

Polymer Type	Percentage	
	Reena et al. (2011)	Freegard et al. (2006)
ABS	57 %	50 – 60 %
HIPS	5 %	20 – 10 %
PC/ABS	5 %	50 – 30 %
PPO	36 %	-
PVC	trace	-

As far as CPUs are concerned, Martinho et al. (2012) investigated the contribution of each type of polymer in all plastic parts of this device using 463 obsolete units. The results are shown in Figure 5. (Martinho et al., 2012).

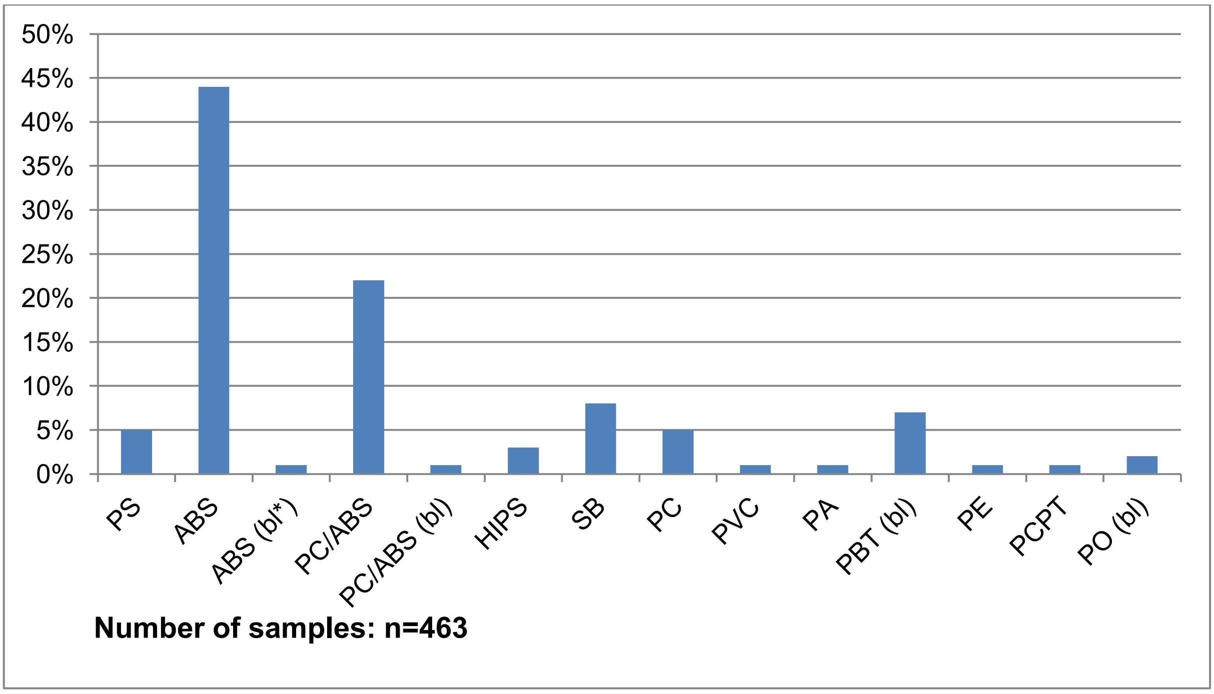


Figure 5: Plastic composition in CPUs (* bl: Blends) (Martinho et al., 2012).

According to this study, ABS (44%) and PC/ABS (23%) are the most dominant types, while PS (5%), styrene-butadiene (SB) (8%), PC (5%) and PBT blends (7%) are found in more than 5% of plastic parts. The contribution of HIPS was found to be relatively low (3%), in contrast with the aforementioned results of the studies of Freegard et al. (2006) and Wäger et al. (2010) regarding computer plastics in general.

Considering microwave ovens, there are several plastic parts, such as the switches, the external plastic on microwave door and the plastic on the inside of microwave door. Novak (2001) reported a content of plastic of about 7 wt. % in microwaves, while generally a deficiency in data about the contribution of each polymer type is observed.

2.3 Flame retardants

2.3.1 Types of flame retardants

Flame Retardants (FRs) are substances used in the manufacture of materials to increase fire resistance in order to ensure safety and to comply with safety regulations. Main applications of FRs are EEE, furniture, cables, insulation boards, textiles and mattresses (Bromine Science and Environmental Forum, 2007; Vehlow et al., 2002). FRs are classified regarding their chemical constitution into the following categories:

- *Inorganic FRs:* This category includes metal hydroxides, such as aluminium hydroxide and magnesium hydroxide, ammonium polyphosphate, boron salts, inorganic antimony, tin, zinc and molybdenum compounds, and elemental red phosphorus. Various inorganic compounds are used as FRs, or as part of a FR system in combination with FRs of the other three categories. Aluminum hydroxide, magnesium hydroxide and inorganic phosphorus compounds are often used as halogen free alternatives to BFRs, while antimony trioxide, zinc borate, zinc hydroxystannate, zinc stannate, and certain molybdenum compounds are used as synergists mixed with different types of FRs. Inorganic FRs slow down the decomposition process (pyrolysis) and the release of flammable gases that support the combustion process by forming a resistant non-flammable layer on the surface of the material. In addition, they release inert gases that contribute by interrupting the chemical chain reaction that results from the production of flames. These FRs are added as fillers into polymers and are considered immobile in contrast to the organic FRs. Except for plastics, they are commonly used in some paints, adhesives, rubber, textile back coatings, wire and cable (American Chemistry Council; Norwegian Pollution Control Authority, 2009).

- *Organophosphorus FRs:* This type includes mainly phosphate esters. In the event of a fire, phosphorus FRs release phosphoric acid which leads the material to char and form a thick layer of carbon, which hinders the pyrolysis process, prevents the release of flammable gases and provides a barrier between the material and the heat source. When not used as alternatives to brominated flame retardants, organophosphorus FRs may contain bromine or chlorine. This type of FRs is used in furniture, foam mattresses, textiles, television casings, rubber and plastics (American Chemistry Council; Norwegian Pollution Control Authority, 2009).

- *Nitrogen-based FRs:* These FRs are usually used in polymers containing nitrogen, such as polyurethane and polyamide. The most widely used FRs in this case are melamines and melamine derivatives. Nitrogen FRs function in several ways, which lead to flame retardancy, either individually or as synergists. At high temperatures, they cause the production of stable molecular compounds that hinder the pyrolysis process and prevent the emission of flammable gases. They also lead to the release of inert nitrogen gases that prevent the reactions leading to combustion. As synergists, they are primarily combined with phosphorus. They are used in insulation, furniture foams and EEE (American Chemistry Council; Norwegian Pollution Control Authority, 2009).

- *Halogenated FRs:* Including a variety of different FRs, halogenated flame retardants (HFRs) are primarily based on chlorine and bromine (Norwegian Pollution Control Authority, 2009). HFRs are the most dominant FRs in EEE plastics given their compatibility and efficiency in a variety of polymer types. Vehlow et al. (2002) report that 30 % of the EEE plastic contains FRs, 41 % of which are halogenated (see Figure 6). The most commonly used HFRs are the brominated flame retardants (BFRs) and are analyzed in the following chapter.

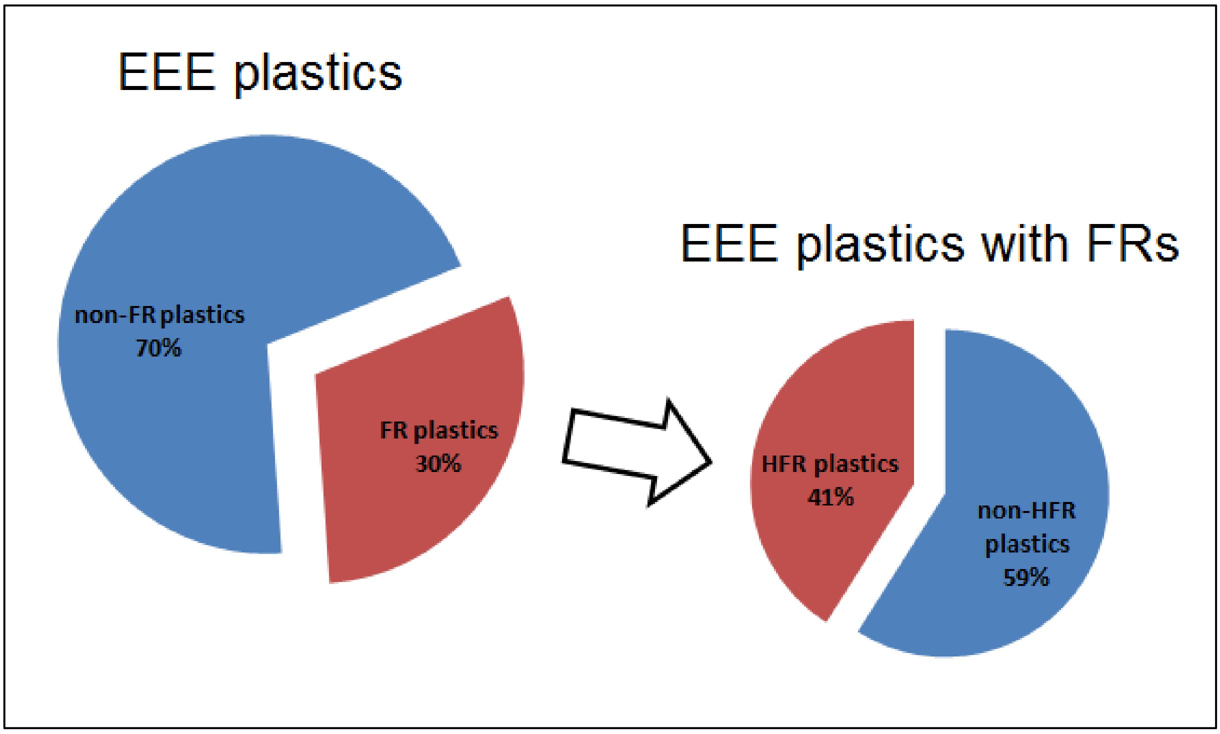


Figure 6: Share of FR plastics in EEE plastics; share of HFR plastics in FR plastics (Vehlow et al., 2002).

2.3.2 Brominated flame retardants

The most commonly used HFRs are based on bromine considering their lower cost and reflecting the need of lesser quantities compared to other types to achieve a high level of fire resistance. Additionally, BFRs have the lowest impact on the polymer's performance compared to the rest of FRs. Regarding EEE, they are usually used in plastic housings and printed circuit boards (Vehlow et al., 2002).

Bromine, and generally halogens, is very effective in capturing the free radicals primarily produced during the flaming combustion. BFRs are thermally labile and release Br• radicals that substitutes the highly reactive H• and •OH radicals and therefore inhibit the radical chain reactions of combustion and the growth of fire. Antimony trioxide (Sb_2O_3) is often used as a synergist, since it increases the halogen release and as a result the effect of fire prevention (Jakab et al., 2003; Zhang et al., 2016).

2.3.3 Types of BFRs

More than 75 brominated flame retardants (BFRs) are commercially available (Gallen et al., 2014). The five major marketed BFRs are:

- Tetrabromobisphenol A (TBBPA)
- Decabromodiphenyl ether (decaBDE)
- Octabromodiphenyl ether (octaBDE)
- Pentabromodiphenyl ether (pentaBDE)
- Hexabromocyclododecane (HBCD)

The most commonly used BFR, containing approximately 59% bromine (Larssen et al., 1999), is TBBPA and it can be used as a reactive FR in printed circuits boards, which means that it does not longer exist as a free chemical in the board, but as a part of the polymeric structure of the resin. It is also used as an additive FR into plastics, mainly in ABS plastic housings, at 13 – 28 wt. %. Furthermore, TBBPA is used as an intermediate in the production of other brominated FR systems, derivatives and brominated epoxy oligomers where it is integrated into the resin as well. (Bromine Science and Environmental Forum, 2012a; Gallen et al., 2014).

DecaBDE, octaBDE and pentaBDE are technical mixtures of polybrominated diphenyl ethers (PBDEs) (Morf et al., 2005), which contain 83 wt.%, 79 wt.% and 70 wt.% bromine respectively (Alaee et al. 2003). PBDEs are a large group of additive BFRs with versatile use in many applications worldwide and are the second highest production group of BFRs currently used (Norwegian Pollution Control Authority, 2009).

HBCD is a white crystalline powder, with 74.7 wt.% bromine (Alaee et al. 2003). It provides a high degree of flame retardancy when used at very low concentrations. It is often found in EEE, but its main application is in polystyrene foam that is used in building construction. In addition, being one of the FR types used to meet the highest levels of fire safety required by legislation for furniture and other textile applications, HBCD is also often applied in the back-coating of textiles, mainly for upholstered furniture (Alaee et al. 2003; Bromine Science and Environmental Forum, 2012b; Gallen et al., 2014).

2.3.3.1 BFRs in EEE plastics

Wäger et al. (2010) reports the different types of EEE plastics, which are more likely to contain FRs. According to their study FRs are found in polymers used in telecommunication devices, computers, monitors, television sets and other consumer and office equipment. FRs are added only in small parts of household appliances and there are some equipment, which are almost always FR-free, such as vacuum cleaners (Wäger et al., 2010).

Several studies report the most possible combinations of BFRs with different types of polymers (Alaee et al., 2003; Freegard et al., 2006; Harju et al., 2009; Wäger et al. 2009; Wäger et al., 2010). Wäger et al. (2010) documents the BFRs, which are usually found in certain polymer types (see Table 4). ABS is considered as the polymer type with the lowest BFR content. DecaBDE is found in most types, while TBBPA is usually found in ABS and HBCD in HIPS. BFRs are rarely found in PVC and in polyurethane (PUR), just as in circuit boards, PentaBDE was widely applied in the past.

Table 4: BFRs usually found in different polymer types (Wäger et al., 2010).

Polymer Type	BFR
PP	DecaBDE, OctaBDE
PE	DecaBDE, OctaBDE
HIPS	DecaBDE, HBCD
PA	DecaBDE
ABS	DecaBDE, OctaBDE, TBBPA
PVC	-
PUR	PentaBDE

Table 5 shows in which polymers is most likely for the five most used BFRs to be found, according to several studies (Alaee et al., 2003; Freegard et al. 2006; Harju et al. 2009; Bromine Science and Environmental Forum, 2012b). From Table 4 and Table 5 it can be deduced that, although TBBPA is the most used BFR, DecaBDE is typically found in the highest number of different polymers, while HBCD, PentaBDE and OctaBDE have been detected in a smaller number of different polymer types.

Table 5: Most likely BFR-polymer combinations (Alaee et al., 2003; Freegard et al. 2006; Harju et al. 2009; Bromine Science and Environmental Forum, 2012b; Morf et al., 2003).

BFR	Polymer	Source
TBBPA	ABS, PS, HIPS, PC	Alaee et al., 2003; Freegard et al., 2006; Harju et al., 2009
HBCD	PS	Bromine Science and Environmental Forum, 2012b
PentaBDE	PUR	Alaee et al., 2003, Morf et al., 2003
OctaBDE	ABS, HIPS	Alaee et al., 2003, Freegard et al., 2006
DecaBDE	PC, PE, PP, PE, ABS,HIPS, PA, PVC	Alaee et al., 2003, Freegard et al., 2006

2.3.3.2 Environmental and health concern of BFRs

As the use of BFRs have been expanding during the last decades and consequently have been introduced into the environment, many studies have investigated their impact on the environment and human health (Zhang et al. 2016, Janssen, 2005; Shaw et al. 2010, Morf et al, 2005; Watanabe and Sakal, 2003). There is a variety of pathways, through which BFRs, and HFRs in general, can enter the environment, such as emission during manufacturing, use, combustion and recycling of the products containing BFRs or leaching from landfills.

During the last decades several studies have reported rising concentrations of some BFRs, both in the environment and in humans (Alaee and Wenning, 2002; Birnbaum and Staskal, 2003, Morf et al., 2005; Shaw et al. 2010). Morf et al. (2005) mention that PBDEs and HBCD have been detected in a wide spectrum of measurements in indoor and ambient air, sewage sludge, sediments, and aquatic and terrestrial wildlife. PBDE congeners were found not only in locations, where they are produced, used or disposed, but also in environmental compartments and biota in remote areas. As a result, considering the potential persistence, bioaccumulation, and adverse health effects of PBDEs and HBCD, there is a huge concern among the scientific community about the negative implications connected with these substances and BFRs in general (Morf et al., 2005).

The main routes of exposure of humans to BFRs are through food intake and inhalation, while dermal uptake is not considered as a major route. Exposure through diet takes place when the substances are persistent enough to be biomagnified in the food chain, while for non-persistent BFRs, the dominant route of intake is inhalation. In case of continuous exposure, BFRs can cause several health impacts because of their toxic characteristics (Sjödin et al., 2003; Watanabe and Sakal, 2003).

Despite the fact that the available data about the toxicity of BFRs are insufficient, some evidence on the toxicity of BFRs and in particular PBDEs is available. The different PBDEs have similar toxicological function and the main target organs are liver, kidney and thyroid. According to available data, mainly from in vitro and animal studies, BFRs potentially have adverse effects on endocrine functions and the central nervous and reproductive systems. The disruption of endocrine functions by BFRs is caused by the interaction of various congeners with estrogen, progesterone and androgen receptors. In addition, BFRs have also been found to inhibit the function of enzymes involved in steroid hormone metabolism (Lyche et al., 2015). Table 6 presents some reported toxic characteristics of the five most widespread BFRs on humans and other species (United States Environmental Protection Agency, 2014; Janssen, 2005).

In addition, many studies argue that there is a connection between BFRs and the emission of dioxins and furans, more specifically of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs) and mixed polybromochloro-dibenzo-p-dioxins and dibenzofurans (PXDD/Fs) (Freegard et al., 2006; Janssen, 2005; Morf et al., 2005; Shaw et al., 2010; Tohka and Zevenhoven, 2002; Zhang et al., 2016). Especially PBDEs, and PBBs, are a considerable source of tetra- to octa-brominated dioxin and furan contamination, which is unintentionally caused during the entire life cycle of these substances (Morf et al., 2005; Shaw et al., 2010). PBDD/Fs and PXDD/Fs can potentially be emitted during BFRs' production, recycling, pyrolysis, gasification, controlled incineration and uncontrolled combustion (Zhang et al., 2016). They are highly toxic substances and their health impacts have been observed in animal studies. According to Shaw et al. (2010) and Birnbaum et al. (2003), these are thymic atrophy, wasting of body mass, lethality, teratogenesis, reproductive effects, chloracne, immunotoxicity, enzyme induction, decreases in T4 and vitamin A, and increased hepatic porphyrins. Additionally, enzyme induction, anti-estrogen activity in human breast cancer cells, and transformation of mouse macrophages into tumor, were the results of in vitro studies (Shaw et al., 2010).

Table 6: Reported toxic characteristics of TBBPA, DecaBDE, OctaBDE, PentaBDE and HBCD (United States Environmental Protection Agency, 2014; Janssen, 2005).

BFR	Toxicity
TBBPA	• In test tube studies, toxic to liver cells and immune (T-cells). May also interfere with thyroid hormone action • Inhibition of brain neurotransmitters in vitro
DecaBDE	• Evidence of neurodevelopmental damage in mice • Evidence of liver and thyroid tumors in rodent studies • Fetal damage observed (delayed hardening of bones, bent limb bones, and weight decreases)
OctaBDE	• Limited toxicity data – animal studies • Increased liver and thyroid weight. Also decreases in thyroid hormone levels • may be a potential teratogen (a prenatal developmental toxin)
PentaBDE	• Evidence of neurodevelopmental toxicity in rodent studies • Decreases thyroid hormone levels • Immune suppression observed on mice with cellular changes in organs critical to immune function • Delay in male and female reproductive development at high doses
HBCD	• Evidence of neurodevelopmental toxicity in rodent studies • Interference with brain neurotransmitters in test tube studies • Limited evidence of interference with thyroid hormone in test tube and rodent studies

Environmental contamination and potential human exposure is almost inevitable during the treatment of BFR-containing materials. Recycling processes of flame-retarded materials, such as extrusion or molding, can not only cause the formation of brominated dioxins and furans but can also lead to a "downcycling" of recycled materials due to the presence of FRs and cause unnecessary human exposure (Shaw et al., 2010; Watanabe and Sakai, 2003). Moreover, higher concentrations of BFRs were measured in e-waste recycling plants compared to other workplace environments, which leads to a high exposure to toxic substances for humans working in such processes (Morf et al., 2005; Sjödin et al., 2001). The combustion of BFR materials can also cause formation and emission of dioxins and furans. The large amounts released during open burning can be prevented with best available technique incinerators; however the cost of these techniques is very high and even then, elevated brominated dioxins and furans concentrations can be found in the bottom ashes. Another option for the treatment of BFR-containing material could be landfilling. However, this practice can also result to a contamination by the leaching of BFRs. Even in properly designed landfills, systems, such as base and capping liners or gas and leachate collection systems, will at some point inevitably degrade and BFRs, due to their persistence, could leach into the soil (Shaw et al., 2010).

2.3.4 Regulations about brominated flame retardants

In this chapter the regulatory framework for WEEE is examined with respect to polymers and FRs. It consists of several regulations, which aim to regulate the treatment of plastics originating from e-waste and to limit and control hazardous substances contained in them. Table 7 summarizes the restrictions regarding the use of the most widespread BFRs.

The WEEE Directive includes a list of mixtures and components, which have to be removed from any separately collected WEEE. This list, set out in Annex VII of the 2012/19/EU Directive includes plastic containing BFRs, meaning that all plastic parts of WEEE containing these substances have to be separated from the WEEE stream before treated (European Commission, 2012).

In order to reduce the environmental impact of WEEE, the EU introduced the 2002/95/EC ''Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment'', which specifies maximum concentration limits for six restricted materials, certain toxic metals and BFRs. It came into force on the 1st of July, 2006 and was renewed by the 2011/65/EU recast, presenting the same concentration limits. The two BFRs, which are restricted by this Directive, are the Polybrominated Biphenyls (PBB), and the PBDEs and the maximum allowed concentration is 1000 ppm (European Commission, 2003a, European Commission, 2011).

The Regulation concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH Regulation) was introduced in 2007 and requires the registration of chemicals in use on the European market. The registration is mandatory if the substances used are classified as hazardous or dangerous and are supplied in certain quantities. The REACH Regulation also includes a list of restricted substances and a list of the Substances of Very High Concern (SVHCs), including dangerous substances, whose use is connected with additional obligations, such as the composition of plans to substitute the SVHC with alternatives having a lower environmental and health impact. The information of other actors in the value chain regarding SVHC substances is also mandatory. Considering BFRs, HBCD, TBBPA and DecaBDE are included in the SVHC list as they have been found to be Persistent Organic Pollutants (POP) and therefore the evaluation of all of them placed in the EU market is mandatory and their suppliers must provide information about them to consumers. Additionally, PBBs are not allowed in articles for skin contact and the use of PentaBDE and OctaBDE has been restricted by the REACH Regulation (maximum concentration 0.1 wt.%) (Baxter et al., 2014; European Commission, 2006; Peeters et al., 2014).

Moreover, the reduction and elimination of the production and use of POPs is subjected by the Stockholm Convention, which also has been ratified by the EU. Certain congeners contained in commercial PentaBDE and OctaBDE and HBCD are considered as POPs and have been added to a list of substances, whose production and use must be eliminated. Furthermore, according to Article 6 of the Convention, waste containing POPs must be managed in a manner protective for the human health and the environment. (Weber et al., 2010; Wäger et al., 2010; Secretariat of the Stockholm Convention, 2001)

Finally, some requirements about certain BFRs are included in the 2003/11/EC Directive (amending for the 24th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations -pentabromodiphenyl ether, octabromodiphenyl ether) and in the 2000/60/EC Directive and its amendments, known as Water Framework Directive (WFD). The first regulation prohibits the placing on the market and the use of pentaBDE and octaBDE and of articles containing one or both of these substances, in order to protect health and the environment (European Commission, 2000; European Commission, 2003c). The WFD entered into force in 2000 and aimed to establish a framework for water protection and management by focusing on planning a strategy for preventing chemical pollution of water. In 2008, the Directive specified a list of 33 substances, some of which should be monitored or reviewed for identification as potentially hazardous substances, while others were identified as priority hazardous substances and should be phased out during the following 20 years. OctaBDE and DecaBDE have been included in the list with the substances to be monitored, while PentaBDE has been regarded as a priority hazardous substance. In 2013 the list was updated and now includes also HBCD as a priority hazardous substance (European Commission, 2000; European Commission, 2008; European Commission, 2013).

Table 7: Restrictions regarding the use of the most widespread BFRs (European Commission, 2003a; European Commission, 2003b; European Commission, 2012; European Commission, 2011; European Commission, 2000; European Commission, 2008; European Commission, 2013; Weber et al., 2010; Wäger et al., 2010; Secretariat of the Stockholm Convention, 2001)

BFR		TBBPA	HBCD	DecaBDE	OctaBDE	PentaBDE	PBB
Regulations	**WEEE Directive (2012/19/EU)**	Separation of BFR plastics from E&E equipment prior to recovery and recycling					
	RoHs Directive (2011/65/EU)	-	-	Max. Concentration 1000 ppm			
	2003/11/EC	-	-	-	Placing on EU market and the use are prohibited		-
	REACH	Evaluation of all chemical substances placed in the EU market. Suppliers must provide information to consumers			Max. Concentration 0,1 wt.%		Not allowed in articles for skin contact
	Stockholm Convention	-	Elimination of the production and use	-	Elimination of the production and use		-
	Water Framework Directive	-	Cessation of emissions in the environment	Establishment of controls of emissions, discharges and losses in the Environment and water quality standards		Cessation of emissions in the Environment	-

2.4 Identification of polymers and flame retardants

The identification of the several polymer types and their additives, such as FRs is of high importance both for research and industrial scale purposes. As discussed in the study of Freegard et al (2006), several methods are used for this kind of identification. Some of them are in the following list:

- Fourier Transform Infrared spectroscopy (FTIR)
- Near infrared spectroscopy (NIR)
- Mid Infrared (MIR) pyrolysis spectroscopy
- Raman scattering spectroscopy
- Mass pyrolysis spectroscopy
- Sliding spark (spark ablation) spectroscopy (SSS)
- X-ray fluorescence spectroscopy (XRF)
- MIR Acousto-optic tunable filter (MIR AOTF) spectroscopy
- Laser induced thermal impulse response (TIR)

- Laser induced plasma spectroscopy (LIPS) spectroscopy, also known as laser induced breakdown spectroscopy (LIBS)
- Gas chromatography – mass spectrometry (GC-MS)

In Chapter 2.4.1 some details about the principles of FTIR are given, as it is the method subjected in the experimental part of the present thesis. In Chapter 2.4.2, 2.4.3 and 2.4.4 some information about NIR, SSS and XRF is reported, considering that these three methods were used in the experimental procedure in order to validate the results of the FTIR method. Finally, Table 8 summarizes the main advantages and disadvantages of some of the aforementioned methods.

2.4.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared (IR) spectroscopy is based on the vibrations of atoms of a molecule. This method provides an IR spectrum by emitting IR radiation, which passes through a sample, and determining which fraction of the radiation is absorbed at a particular energy. The energy, at which any peak in an absorption spectrum appears, corresponds to the frequency of a vibration of a part of a sample molecule. IR spectroscopy is a popular technique for characterization of polymers, including identification of their composition, monitoring of polymerization processes, characterization of polymer structure, examination of polymer surfaces and investigation of degradation processes. The most important advantages of this method appeared with the introduction of Fourier transform infrared (FTIR) spectrometers, which use an interferometer and the mathematical method of Fourier-transformation (Seidel, 2008; Sullalti, 2012).

The basic principle of FTIR spectroscopy is the interference of radiation between two beams, which results to an interferogram. An interferogram is a signal produced as a function of the change of pathlength between the two beams. The two domains of distance and frequency are interconvertible by the Fourier-transformation (Stuart, 2004; Seidel, 2008).

Figure 7 shows schematically the basic components of a FTIR spectrometer as reported in the publication of Stuart (2014). The radiation emitted from the source passes through an interferometer before reaching the sample. Most interferometers use a beamsplitter, which receives the incoming infrared beam and divides it into two optical beams. The one beam reflects off of a mirror which is stable and the other reflects off of a mirror which is based on a mechanism which allows it to move a very short distance of a few millimeters away from the beamsplitter. So the two beams, after reflecting off of the mirrors, are recombined when they reach the beamsplitter. Because the path of the one beam is of fixed length and the path of the other is constantly changing as its mirror moves, the signal generated by the interferometer is the result of these two beams "interfering" with each other and therefore is called interferogram. After passing the sample, the radiation reaches a detector and then an amplifier, where amplification of the signal takes place, in which high-frequency contributions are eliminated, the data are converted to digital form by an analog-to-digital converter and end up to the computer for Fourier-transformation. After the transformation the computer presents the spectral information in form suitable for analysis (Stuart, 2004; Thermo Nicolet Corporation, 2001).

Figure 7: Basic components of a FTIR spectrometer (Stuart, 2004)

With the use of Infrared (IR) spectroscopy it is possible to obtain spectra from a variety of solids, liquids and gases. Although no significant preparation is needed, in many cases some samples have to be shortly processed in order to obtain a good quality of results. Traditionally, the way of analyzing by IR spectrometers has been by means of transmitting the IR radiation directly through the sample. For liquid or solid samples the intensity of the spectra is dependent on the thickness of the sample and typically the thickness cannot exceed a specific extent of a few tens of microns. In recent years the technique of Attenuated Total Reflectance (ATR) has been developed and used to analyze solid and liquid samples, because it combats the sample preparation and spectral reproducibility of FTIR analyses, which have been the most significant drawbacks of the technique of transmission. (Perkinelmer, 2005).

ATR utilizes the phenomenon of total internal reflection. A beam of radiation is directed onto an optical dense crystal and by entering it will undergo total internal reflection when the angle of incidence at the interface between the sample and crystal is exceeding the critical angle. The angle is a function of the refractive indices of the two surfaces. The evanescent wave, created by the internal reflection, extends beyond the surface of the crystal into the sample, which is held in contact with the crystal. The material of the sample selectively absorbs radiation and the beam loses energy at the wavelength where the material absorbs. The resultant attenuated radiation is measured and plotted as a function of wavelength by the spectrometer and provides the desired information about the absorption spectral characteristics of the sample (Perkinelmer, 2005; Stuart, 2004). It must be noted that two requirements must be met in order to have a successful analysis by ATR:

- The sample must be in contact directly with the ATR crystal, because the evanescent wave penetrates only a few microns (0.5 µ - 5 µ) into the sample.
- The refractive index of the crystal used must be significantly greater than that of the sample. Otherwise, internal reflectance will not occur, because the light will be transmitted rather than reflected in the crystal. There are a number of crystal materials available for the ATR technique. Zinc Selenide (ZnSe) and Germanium are commonly used, while diamond is by far the best ATR crystal material because of its robustness and durability (Perkinelmer, 2005).

FTIR spectroscopy has some important advantages with reference to other spectrometric measurement methods. The main strengths are:

- The Fellgett or multiplex advantage referring to the simultaneous measurement of all frequencies leading to an analysis, which lasts a few seconds than several minutes.
- Sensitivity is significantly improved with FTIR, because of the features of the detectors, the higher level of optical throughput resulting in a substantial gain in energy and much lower noise levels (known as the Jacquinot or throughput

advantage), and the fast scans, which enable the coaddition of several scans in order to reduce the random measurement noise to any desired level.

- The speed advantage. The moving mirror covers short distances rapidly, and this, in combination with the Fellgett and Jacquinot advantages, offers the possibility to obtain spectra on an extremely short time (millisecond timescale) (Jozwicki and Rataj, 1998; Thermo Nicolet Corporation, 2001; Stuart, 2004).

2.4.2 Near Infrared Spectroscopy (NIR)

Near Infrared spectroscopy is a relevant method for identification of polymers as it is a non-destructive and fast technique. It covers the wavelength range adjacent to the mid infrared and up to the visible region (Reich, 2005). The basic principle of the NIR technology is the diffuse NIR reflection spectroscopy, where the characteristic absorption behaviors of different polymer types in a typical spectral region are used. The sample is radiated with an IR light and the reflected light is analyzed using a NIR detector array (Seidel, 2011).

NIR spectroscopy presents a lot of advantages: remote high speed measurements, high penetration depth of the NIR radiations preventing a sample pretreatment, and an important signal-to-noise ratio. It is more adapted than MIR to automatic sorting, as spectrum acquisition is faster. The accessibility of NIR sensors led to the further development of this technique. The main disadvantages of this method are the incapability to detect black samples, due to the fact that radiation is totally absorbed and the size and the shape of the samples must fulfill some specific requirements. In addition, NIR absorption is weaker and featureless than in the case of MIR (Beigbeder et al., 2013; Chancerel and Rotter, 2009).

2.4.3 Sliding Spark Spectroscopy (SSS)

Another technique used for identification of plastics and their additives is the Sliding Spark Spectroscopy (SSS). It is based on the thermal vaporization of a small amount of the plastic surface using a chain of defined high-current sliding sparks. The material components in the spark plasma are vaporized, atomized and activated to emit radiation. After that the emitted radiation is measured and the spectrum is analyzed. SSS also utilizes electrical information to achieve the identification of polymers and contained additives (Becker and Eisenreich, 2006; Seidel, 2011).

SSS is a fast and non-destructive method. However, for the measurement with SSS the samples must be pressed against the sensor. Therefore an automation of this detector system is complicated. Nevertheless, the SSS offers a wide area of applications and is a viable measurement principle for plastic characterization, but specialized for spot checks (Becker and Eisenreich, 2006; Peeters et al., 2015).

2.4.4 X-ray fluorescence spectroscopy (XRF)

X-ray fluorescence spectroscopy is an analytical method used to determine the chemical composition of a vast variety of materials in solid, liquid, powder or other form (Brouwer, 2003). During a measurement, X-rays are produced by a source, which usually is an X-ray tube, and irradiate the sample. When the sample is bombarded with radiation, vacancies may occur from the removal of inner orbital electrons. As a result, electrons are transferred from outer to inner electron shells, in order to regain stability of atoms. These transitions are accompanied by emission of an X-ray photon having energy equal to the energy difference between the two states. The X-ray emission wavelengths are characteristic of the atom in question. Thus, when a sample is made up of many different types of atoms, each atom will produce a series of wavelengths, and all of the contributions add up to become the total X-ray emission from the sample. Utilizing the diffracting power of a single crystal, or the proportional characteristics of a photon detector, XRF is able to separate the polychromatic beam of radiation from the sample into separate wavelengths, allowing qualitative and quantitative elemental analysis (Brouwer, 2003; Jenkins, 2000).

XRF is a fast, simple and non-destructive method, which requires a minimum of sample preparation (Aldrian et al., 2015; Brouwer, 2003; Gallen et al., 2014). Although it is not able to identify the type of BFR compounds, it can be used for detection of bromine with a detection limit of 10 ppm to 100 ppm. Portable handheld XRF instruments, which limit the time requirement for a measurement to less than a minute, provide a rapid-screening analytical approach for identification of the presence of BFR and separation of polymers containing bromine (Aldrian et al. 2015; UNEP, 2012).

The main advantages and disadvantages of the methods described above according to literature data are summarized in Table 8.

Table 8: Main advantages and disadvantages of FTIR, NIR, SSS and XRF (Aldrian et al., 2015; Becker and Eisenreich, 2006; Beigbeder et al., 2013; Chancerel and Rotter, 2009; Freegard et al., 2006; Harju et al., 2009; UNEP, 2012; Tohka and Zevenhoven, 2002).

Method	Advantages	Disadvantages
FTIR	• Reliable technology • Non-destructive	• Surface impurities can influence the result • The surface of the object should therefore be relatively flat
NIR	• Fast, non-intrusive • High penetration depth of the NIR radiations, which prevents a sample pre-treatment • Automation possible	• No identification of black samples • Particle size and shape must fulfill the requirements
SSS	• Fast, non-intrusive • Identification of additives	• Not suitable for an automated sorting facility
XRF	• Non-destructive • Rapid and simple analysis	• Non-specific for individual substances • Quite expensive

2.5 Treatment of WEEE polymers

2.5.1 Recycling methods

Taking into account the environmental problems connected with the management of WEEE and the variety of valuable materials contained in them, the EU included in

Directives 2002/96/EC and 2012/19/EU quotas of WEEE, which have to be recovered in the form of energy and/or materials. These quotas are very ambitious as they have a range of 55 – 80 % for recycling 70 – 85 % for recovery (Achilias and Antonakou, 2015; European Commission, 2003b; European Commission, 2012). Considering the high polymer content in WEEE, plastics are a very important issue to increase the recycling potential and to achieve the aforementioned quotas (Beigbeder et al., 2013).

Several methods of plastic recycling exist. The main methods, according to Achilias and Antonakou (2015) are:

- Mechanical recycling
- Feedstock recycling
- Energy recovery

Mechanical recycling refers to recycling processes based on physical phenomena, through which a secondary raw material is produced from plastic. These processes include cleaning, size reduction and separation into the mixture components, melting and then reforming (Achilias and Antonakou, 2015; Beigbeder et al., 2013).

Feedstock recycling refers to the production of either the initial monomers or fractions of oligomers by breaking the polymeric bonds. Depolymerization can be achieved either chemically (chemical recycling) or with the use of heat (thermolysis). The product of this method is considered to be of higher quality and value compared to the products of the other recycling methods (Achilias and Antonakou, 2015; Beigbeder et al., 2013). However, while technically feasible, feedstock recycling is reported to be uneconomical without significant subsidies because of the low price of petrochemical feedstock compared with the plant and process costs related to the production of monomers from waste plastic (Aguado and Serrano, 1999; Hopewell et al., 2009).

Energy recovery is concerned with the energy production from plastic waste and it includes primarily incineration. This technique exploits the high calorific value of polymers. An important disadvantage of this method is the potential emission of a series of dangerous byproducts, such as dioxins and furans, mainly through incineration (Achilias and Antonakou, 2015; Beigbeder et al., 2013). However, incineration plants equipped with flue-gas cleaning technology emit practically no dioxins and furans into the atmosphere (Gottschalk et al., 1996; Hartenstein and Licata, 2000).

2.5.2 Challenges

Several studies report that the recycling of WEEE plastic is facing many challenges. Firstly, the plastic mix found in WEEE is characterized by a high complexity due to the existence of more than 300 types of plastics in this material stream. As a result, most types are present only in small amounts, which makes the development of advanced recycling operations difficult and decreases the efficiency of the recycling processes (Peeters et al, 2014; Peeters et al., 2015). Secondly, WEEE plastics may contain organic and inorganic hazardous substances and therefore the achievement of certain quality standards of the secondary material is challenging (Schlummer et al., 2007). The WEEE Directive requires the removal of plastic containing BFRs from the separately collected WEEE (European Commission, 2012), which is a difficult mission, as the development of methods for identification of BFRs in a large scale is insufficient. Labels indicating the types of used polymers and BFRs (such as code numbers for Flame Retardants according to DIN EN ISO 1043-4, see Appendix A) on plastic would help increasing the efficiency of the recycling processes. However, some studies have reported a deficiency of labels or mismarking on an important part of WEEE plastics and consequently it cannot be assumed that those without the FR abbreviation do not contain FRs. Additionally, FR marks on plastics refer to the presence of FRs but with no indication of the concentration and often not even the type applied (Freegard et al., 2006; Martinho et al. 2012; Peeters et al., 2014).

2.5.3 Treatment of FR plastic

Some laboratory tests showed that FR-containing plastics can be recycled, presenting a degradation of mechanical properties and flame resistance depending on the used FR and stabilizer compounds (Cefic-EFRA, 2006; Dawson and Landry, 2005; Imai et al., 2002). However, in most of these tests, virgin non-recycled materials were used and were tested only on laboratory scale, while knowledge about the separation of FR-containing plastics -aiming to achieve efficient recycling processes-, in this case originating from the partly recycled, evolving and complex mix of polymers found in WEEE, still remains insufficient (Peeters et al., 2014).

Mechanical processing and recycling of BFR plastics may be accomplished including selective disassembly, shredding, magnetic and eddy current separation, in order to gain a metal-rich fraction and a fraction of combustible polymers. Feedstock recycling of WEEE containing BFRs may also be partly achieved by mechanical methods although it is reported that feedstock recycling by thermal cracking (pyrolysis) is receiving increasing attention, due to the potential recovery of a high percentage of monomers or secondary valuable materials, leading to a more sustainable waste management (Achilias and Antonakou, 2015; Tohka and Zevenhoven, 2002). Thermal processing in conjunction with metallurgical processing of the fractions gained by mechanical processes of e-waste is currently considered to be the most effective option to combine the recovery of precious metals and energy with the destruction of some hazardous substances. However, all the aforementioned techniques may be hindered because of the presence of BFRs, due to their environmental and health impacts mentioned in Chapter 2.3.3.2 and the reduced secondary material quality. For example, the use of recycled ABS as a blend with PC is not possible as a result of the depolymerization of PC caused by the BFRs, resulting in poor quality of the product. Additionally, regarding thermal processing, the main challenge is the formation of toxic substances, such as brominated dioxins and furans (Tohka and Zevenhoven, 2002).

There is a rising interest from the bromine industry in recovery of bromine from WEEE through thermal treatment. The recovery is possible by isolating bromine from the gas stream. The isolation is based on absorption into an aqueous (hydroxide) solution, where the hydrogen bromide in the product gas is neutralized and converted into salt. Alternatively, a hydrobromic acid solution can be produced as a product. The bromine loop is then closed, when the bromine salts or other residues are utilized by the bromine industry by converting them into bromine products (Tohka and Zevenhoven, 2002).

Nevertheless, as mentioned in Chapter 2.3.4, the legislation relating to BFRs, specifically the RoHS Directive, the WEEE Directive and the EU regulation on Persistent Organic Pollutants or POPs (850/2004) place several restrictions on the treatment of BFR plastics. In addition with the restriction of the use of some BFRs, the separation of BFR plastic from the WEEE stream is mandatory, aiming to the complete elimination of those substances over time (Baxter et al., 2015). To achieve this goal, without taking into account the export of WEEE plastics containing FR outside Europe, due to its illegality, the only realistic option according to Baxter et al. (2015) is the permanent destruction of this kind of plastics through incineration with energy recovery. However, even this option requires a separation of FR plastics from the recyclable stream. Considering the economic and environmental implications of the insufficient separation leading to a loss of pure and valuable plastics in the FR plastic fraction, the development of efficient practices is of high importance (Baxter et al., 2015). As Peeters et al. (2014) mention, little is known on the feasibility of separating FR-containing plastics of the e-waste plastic stream, which is characterized by a high and evolving complexity, for the purpose of further treatment, such as closed loop recycling. Previous work on this topic is presented in the following chapter.

2.5.4 Previous Work

Several studies have investigated WEEE to the purpose of treatment of FR plastic by using different methodologies. Some of them aimed to support the design and the operation of recycling processes by analyzing and forecasting the trends in the evolution of the material composition of WEEE (Chancerel and Rotter, 2009; Peeters et al., 2015), others by testing and comparing the efficiency of different methods for identification and separation of FRs in WEEE (Aldrian et al., 2015; Freegard et al., 2006; Gallen et al., 2014; Ghosal and Fand, 2015; Peeters et al. 2014) and others just by measuring or identifying the FR content of several WEEE types and providing knowledge about the contaminants in WEEE (Chen et al., 2012; Reena et al., 2011). Some of those studies and their results are discussed in this chapter.

Peeters et al. (2014) investigated two different separation scenarios for WEEE plastics:

- A “disassembly” scenario, which is based on the identification and manual separation of plastics, using a combination of techniques, such as using in-mould labels, manufacturers’ information or NIR and FTIR hand scanners.
- A “size-reduction” scenario which is based on shredding and screening followed by automated optical sorting and density-based separation processes.

The study of Peeters et al. (2014) focused on the recyclability of non-POP plastics, but according to Baxter et al. (2015) the techniques investigated have the same implications for the separation and selective removal of FR plastics. Baxter et al. (2015) also claim, that, although the study of Peeters et al. (2014) was applied to flat screen displays and considering the separation of PC/ABS plastics containing organophosphorus FRs, it seems that the conclusions can be generalized to other types of plastic and to BFRs.

On the one hand, for the size-reduction scenario, two drawbacks were found. Separation efficiency is challenged by density overlaps between different fractions, and optical separation by the use of NIR by the black plastics in the waste stream, which cannot be identified with this method. These challenges affect both yields and purities in the separation process. Although FRs are effectively eliminated, a yield of only around 70% by mass was reached, which means that 30% of the initial plastic stream, the majority of which is “clean” (FR-free), is “lost” by sending it for incineration. Moreover, the recovered FR material stream is only around 80% pure (PC/ABS with organophosphorus FRs), which means that it still contains 20% FR-free polymers (Baxter et al. 2015; Peeters et al., 2014).

On the other hand, the disassembly scenario achieved a more effective separation, with potentially recyclable plastics in compliance with the RoHS requirements reaching purities even exceeding 99%. Although a slight degradation in certain properties and occasional deformations regarding certain aesthetic factors were observed, the recyclable plastics were considered commercially approved (Baxter et al. 2015; Peeters et al., 2014).

Another study, which aimed to ease the separation of plastics contaminated with bromine originating from BFRs from the WEEE stream, is that from Aldrian et al. (2015). The logic of this work was similar to this of the present thesis, as it tested the suitability of a Field portable X-ray fluorescence (XRF) device in the characterization of WEEE plastics in regard to BFRs. Casings from TVs and personal computers were investigated in sites of a waste management company. The bromine content of every sample was determined using the aforementioned device and it was possible for the operator to decide if each material was suitable for recycling instantly, because the concentration results were provided instantly on the display of the device. If the bromine content of a polymer was higher than the specified limit value of 300 ppm, it was sorted out and collected separately to dispose them of. Polymers with lower bromine content than the limit value represented the recyclable fraction. The recyclable fraction was additionally sampled by cutting out a 10 x 10 mm square and was lead to a further reference analysis with GC-MS. The samples were homogenized and analyzed regarding the content of PBBs and PBDEs. This approach can be seen schematically on Figure 8 (Aldrian et al., 2015).

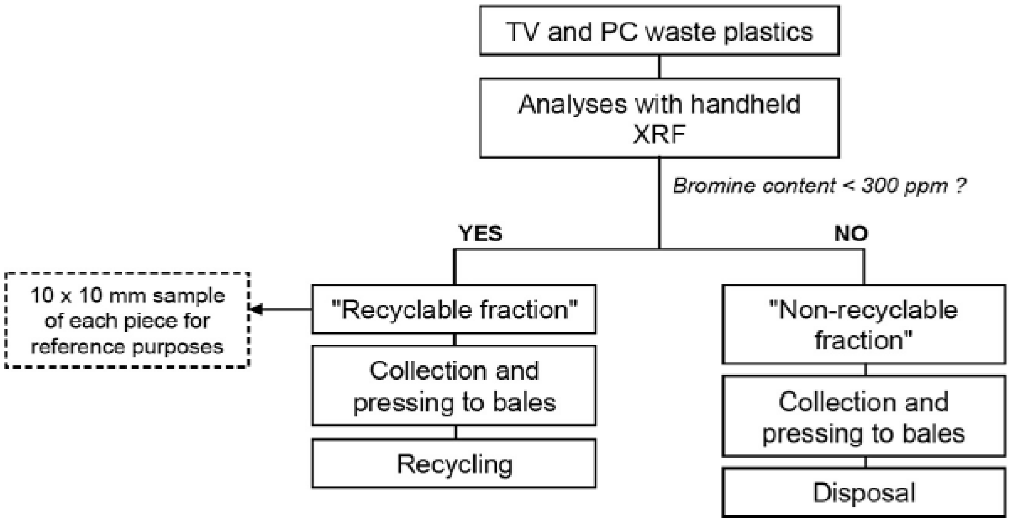


Figure 8: Overview on the monitoring and sampling procedure in the work of Aldrian et al. (2015).

Aldrian et al. (2015) confirmed the presence of BFRs in the examined stream of TVs and PC monitors during an examination of over 3000 pieces of TV waste plastics and almost 1600 pieces of PC waste plastics. As the main aim of this study was to find an efficient method for monitoring of BFRs in TV and PC waste plastics on site, Aldrian et al. (2015) conclude that the handheld XRF provides a fast screening of large volumes of polymers and therefore it seems to be a quite effective equipment for monitoring purposes. They report that for the limit value of 300 ppm, precision and accuracy of XRF were sufficient and since the measurement error improves with higher concentrations, any target limit value higher than 300 ppm is achievable. Concluding, they highlight the need for monitoring measures to identify the plastics with contents of BFRs higher than 50000 ppm in order to prevent the contamination to the recyclable fraction. As the percentage of contaminated pieces was found quite high, they infer that the effectivity and economic viability of recycling the personal computer plastic waste stream is questionable (Aldrian et al., 2015).

Gallen et al. (2014) also test the use of XRF technology, as well as the use of surface wipe test, for the identification and quantification of BFRs in plastics of consumer products, the majority of which used in the framework of this study were EEE. The surface wipe test is a method covering the identification and quantification of substances on the surface of a solid sample. In the study of Gallen et al. (2014), surfaces of plastic samples were wiped with special wipes, which were then analyzed using extraction with dichloromethane (DCM), ultrasonication and filtration, followed by analysis using liquid chromatography tandem mass spectrometry (LC-MS/MS) considering the content of TBBPA, HBCD and PBDE congeners.

Furthermore, they aimed at validating non-destructive against destructive chemical analysis, in order to determine if they are a fast and effective alternative for the identification of specific BFRs and predicting their concentrations in plastics originating from consumer products. As discussed in their work, with the increasingly control of several BFRs, a fast method to provide regulators information on whether these chemicals are present in consumer products and to identify BFR-containing plastics in the recycling stream may be helpful in eliminating BFRs in products and in complying with the regulations (Gallen et al., 2014).

Gallen et al. (2014) conclude that the combination of XRF with the wipe testing strategies can be an effective tool in identifying the presence of some BFRs, including c-octaBDE congeners, BDE-209 and TBBPA, in a wide range of consumer products. Moreover, they determined some product types that are likely to contain BFRs through the XRF screening, including some sWEEE, such as personal computers (Gallen et al., 2014).

Freegard et al. (2006) in their work discussed the effectiveness of techniques available for identification of different polymer types and BFRs contained in them. The aim was to find out which of these techniques are suitable for use on automated sorting lines and review the capabilities of a selection of commercially available state of the art polymer identification and BFR detection instruments.

The authors after an empirical review on several available techniques, including automated sorting systems using TIR, XRF, NIR, FTIR, Raman, LIBS and SSS, found out that surface ablation by LIBS or sliding spark spectroscopy and FTIR appear to be the most suitable for BFR detection with XRF in third place. Purposebuilt commercial instruments, aimed both in terms of cost and practicality at the recycling industry, have been produced using these three methods. The instruments in question are SlideSpec (SSS), PolyAna (FTIR) and Niton XLt (XRF) and are similar in size, cost, sampling speed and ergonomics of use and according to the authors appear to set the benchmark for this application (Freegard et al., 2006).

The studies discussed above are just some examples of work on the topic subjected in this thesis. Despite the raising awareness on this topic, there are huge knowledge gaps, which make the continuous research by the scientific community essential. In this sense, this thesis aims to provide useful data for the identification and separation of FR plastics. More detailed results of some other studies about the identification and measurement of polymers and FRs will be presented in Chapter 3.2, in order to compare them with the results of the experimental part of the present work.

3. EXPERIMENTAL PART

3.1 Experimental procedure

3.1.1 Material and methods

For the purpose of this study, plastic housings of CPUs and microwave ovens have been investigated in regard to the used polymer types and FRs. The experimental procedure consisted of three parts: the sampling, the sample preparation and the analysis of the samples, which are described in the following sections. The sample analysis included the main analysis with the use of Fourier Transform Infrared spectroscopy (FTIR) and a reference analysis with the use of Near Infrared Spectroscopy (NIR), Sliding Spark Spectroscopy (SSS) and X-ray fluorescence spectroscopy (XRF), in order to validate the FTIR measurements. Figure 9 shows the steps of the experiment schematically. The results of the FTIR analysis are then interpreted (Chapter 3.2) in order to extract conclusions about the performance of this method in identification of polymers and FRs and the presence of FRs in personal computers' and microwave ovens' plastic housings (Chapter 4).

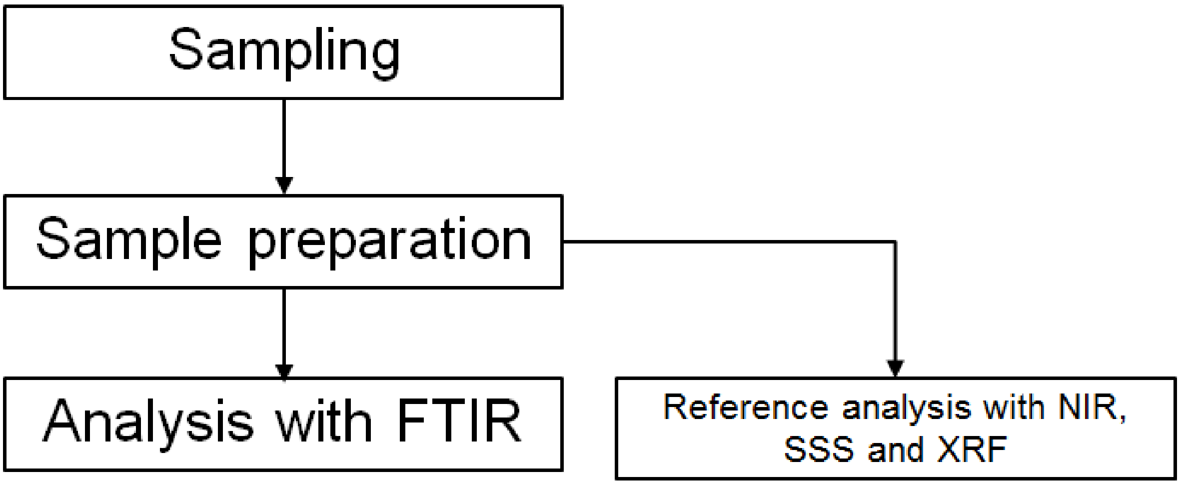


Figure 9: Schematic overview of the experimental procedure.

3.1.2 Sampling

Plastic housings of 7 Personal computers (Central Processing Units – CPUs) and 12 microwave ovens were obtained from Demontage- und Recycling Zentrum (DRZ), which is a Recycling, Reuse and Upcycling Company for WEEE in Vienna. The computers and microwave ovens were already dismantled by personnel of the company and examples of the housings obtained are shown in Figure 10.

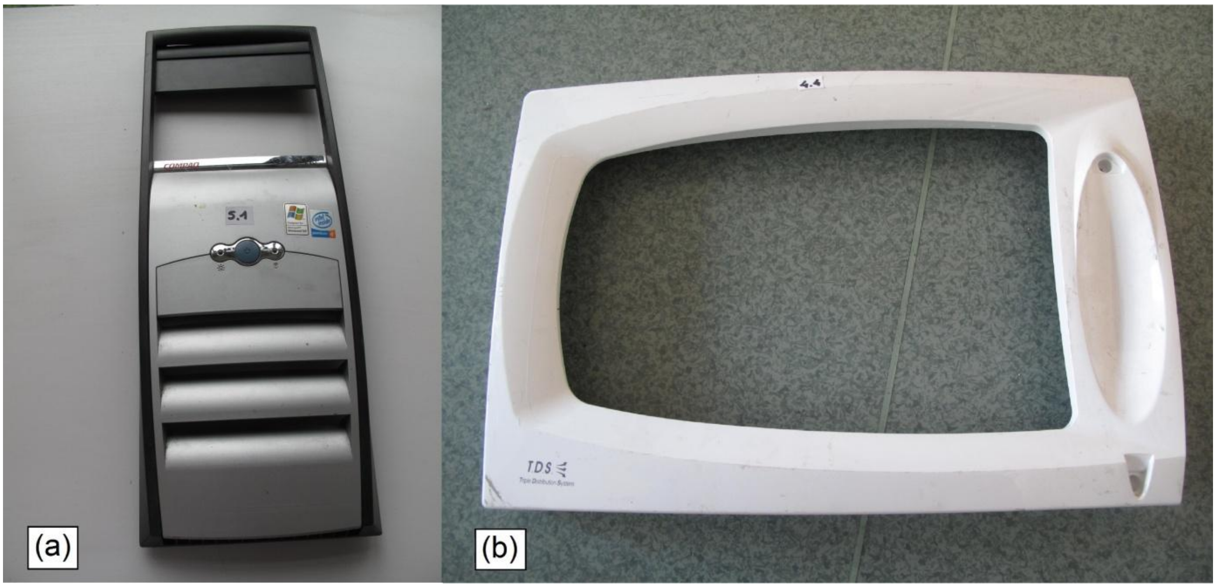


Figure 10: Plastic housings of (a) CPU and (b) microwave oven obtained by DRZ.

3.1.3 Sample preparation

Initially, the plastic parts obtained were examined to assess if they possessed a moulding mark providing manufacturers' information about the polymer types and FRs contained in their products. Figure 11 shows an example of a mark indicating ABS on a plastic housing of a microwave oven. All existing marks were recorded (see Appendix D and Appendix F).

Figure 11: Label found on microwave oven's plastic housing indicating ABS.

Consequently, the plastic housings were cut into pieces of approximately 7cm x 7cm, in order to analyze them by NIR, SSS and XRF. Smaller samples would be hard or even impossible to be measured by the miroSpark analyzer, which was used for the

NIR and SSS analysis. Two samples of each plastic housing were prepared. The preparation included the use of several tools, such as hammers, pliers and hacksaws. For some of the samples, removal of coatings and paints was necessary in order to obtain more reliable results. This was possible with the use of knifes and rasps.

For the FTIR analysis the samples should be flat in order to achieve a good contact between the spectrometer and the sample. Samples which were not flat were cut into pieces of approximately 1cm x 1cm, in order to achieve the maximum flatness. Flat samples could be bigger than 5cm x 5cm. The roughness of the plastic parts is another parameter, which affects the results of the FTIR analysis. Samples with rough surface would not have the desired contact with the spectrometer and therefore were processed with knifes and rasps, in order to make the surface smooth. Finally, coatings and paints were removed.

After the preparation, all samples were labeled with numbers, in order to facilitate the further procedure. Figure 12. shows some examples of the appearance of the samples analyzed by NIR, SSS, XRF and FTIR.

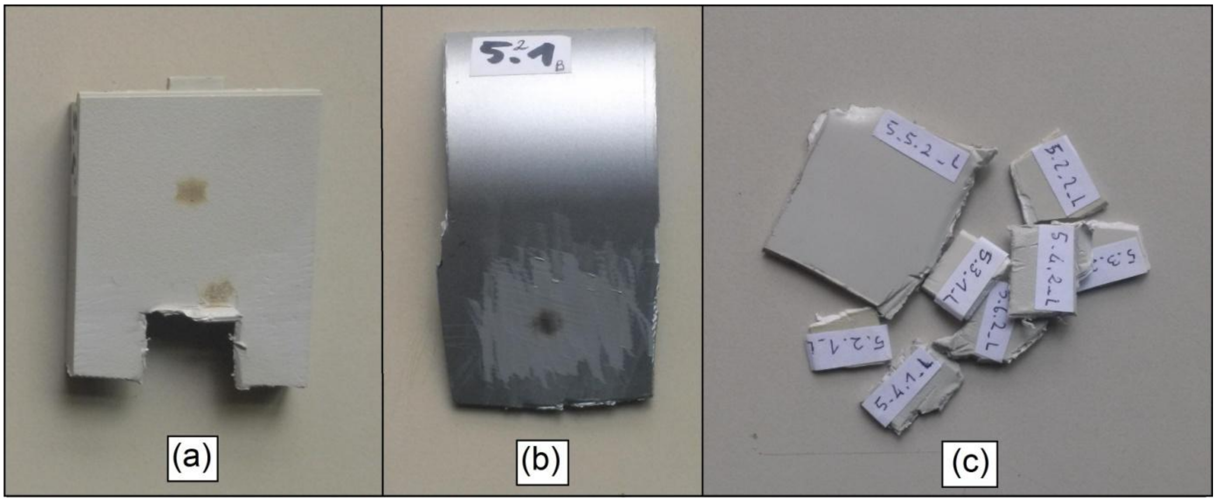


Figure 12: Examples of samples analyzed by FTIR, NIR, SSS and XRF: (a) Sample with size approximately 7cm x 7cm, (b) Sample with size approximately 7cm x 7cm after removal of paint, (c) Samples, which were not flat, cut into pieces with size approximately 1cm x 1cm for FTIR analysis.

3.1.4 Sample analysis

As mentioned before, all samples were analyzed by FTIR, as it was the technique in question, and by NIR, SSS and XRF, in order to obtain reference data about the measured samples and to be able to validate the FTIR results. The reference analysis and the FTIR analysis are described in Sections 3.1.4.1 and 3.1.4.2 respectively.

3.1.4.1 Reference analysis

The samples prepared in the previous step, were analyzed using the miroSpark by IoSys, which combines a mobile NIR spectrometer and a Sliding Spark Spectrometer (see Figure 13), and the xSORT handheld XRF analyzer by SPECTRO (see Figure 14). Each sample (two of each device) was analyzed once with each reference method (n=14 for CPUs and n=24 for microwave ovens).

Figure 13: MiroSpark by IoSys.

3.1.4.1.1 Analysis with NIR and SSS

The left pistol seen in Figure 13 is the NIR pistol. This method is able to identify the polymer type of the samples in question. Each sample was measured by the sensor in front of the pistol with measurement duration of less than three seconds. The result of the analysis was immediately shown on the screen of the miroSpark device. The SSS pistol is located on the right of the device (see Figure 13). The measurement with this method lasted approximately 5 seconds per sample and the results of polymer identification, as well as the concentration of included inorganic elements, such as bromine, were instantly visible on the screen.

3.1.4.1.2 Analysis with XRF

The xSORT handheld XRF analyzer by SPECTRO is a portable spectrometer, which is able to identify and measure inorganic elements and their concentrations in the measured sample. Each analysis lasted approximately 30 seconds and the results were given in % wt. on the screen. The element in question during the identification of inorganic elements by XRF, as well as by SSS, was bromine, the presence of which above a specific limit can be used as an indication of contained BFRs in the plastic housings.

Figure 14: xSORT handheld XRF analyzer by SPECTRO.

3.1.4.2 *Analysis with FTIR*

After completion of the reference measurements, all samples were analyzed by the use of an Alpha FTIR Spectrometer with a Platinum ATR module using the high pressure sampling variant by Bruker (see Figure 15). The OPUS software by Bruker was used for the needed measurements. Each side of the plastic samples was measured separately, in order to increase the reliability of the results and test the reproducibility of the technique in question. This led to a total number of 28 measurements for CPUs and 48 measurements for microwave ovens (n=28 for CPUs and n=48 for microwave ovens).

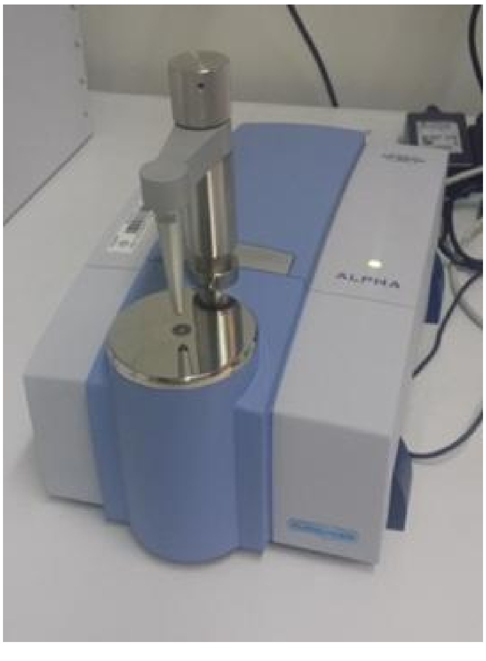


Figure 15: Alpha FTIR Spectrometer with a Platinum ATR module using the high pressure sampling variant by Bruker.

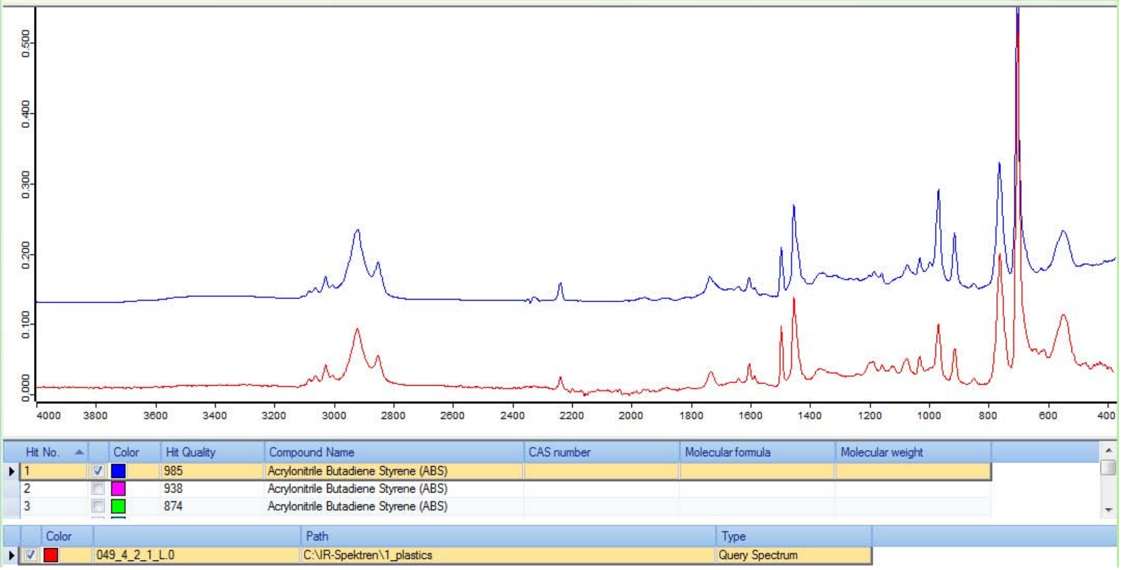
The measurement of each sample consists of few simple steps leading to a duration of 1 to 3 minutes per sample. The basic steps are the following:

- Cleaning the ATR crystal with the use of ethanol or acetone, in order to avoid impurities caused by previous samples or other sources, which could affect the result.
- Measuring a background spectrum, which is obtained by running a measurement without any sample on the ATR crystal. This kind of measurement is also called reference measurement and lasts a few seconds.
- Placing the sample on the ATR crystal, and pressing it with the anvil by adjusting the pressure arm in order to achieve a perfect contact between the sample and the crystal. When a good contact is impossible, further preparation of the sample is required, including for example cutting into smaller pieces or smoothing with the use of a knife or a rasp.
- Measuring the sample spectrum. The duration of the measurement depends on the number of scans set as a parameter. In this experiment 30 to 64 scans per measurement were done, lasting 30 to 60 seconds.
- Acquiring and saving the spectrum for evaluation.

For the identification of polymers and FRs two different identification software types were used: the OPUS/SEARCH and the IDENT.

The OPUS/SEARCH allows the identification of unknown spectra by comparing them to spectra libraries. The libraries used in this method were the BPAD library for the basic polymers and the IR - Flame Retardants - Bio‑Rad Sadtler IR Spectra Database for flame retardants. After the measurement, the OPUS/SEARCH carries out a comparison between the measured spectra and those contained in the libraries and presents the most similar in an order of similarity. The spectra contained in this list are available for further analysis and interpretation. Figure 16 shows and example of an analysis by the OPUS/SEARCH, where the obtained spectrum (red colour) is compared with an ABS reference spectrum proposed by the OPUS/SEARCH. As seen in Figure 16, after measuring each sample, the results of the analysis are listed beneath the measured sample. The software sets a list of spectra in order of similarity to the obtained spectrum measured in terms of hit quality, expressing the similarity to the measured spectrum. A hit quality was considered as satisfying if its values exceeded 850.

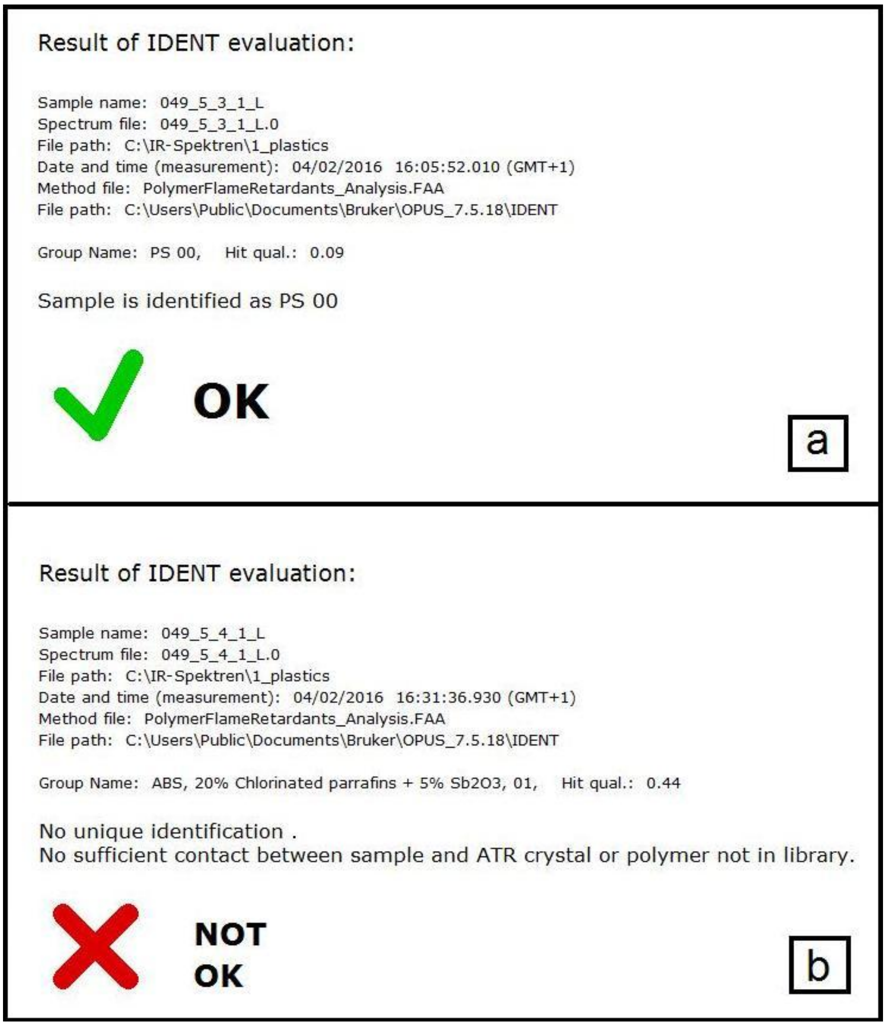
The IDENT software, after the measurement, automatically checks a measured spectrum with spectra of the IDENT-library in terms of compliance. The analysis result is the identified polymer and FR, but, in contrast to the OPUS/SEARCH software, there is no possibility to show the reference spectra for detailed comparison and interpretation. In cases where the obtained spectra is assigned to a spectrum of the library, a message "OK" and the identified polymer type, as well as the flame retardant, are shown on the screen. In cases, where the spectra cannot be identified, due to a not sufficient contact between the sample and the ATR crystal or an absence of a polymer type in the library, a message "not OK" is displayed (see Figure 17). The library includes the most common polymer/FR-combinations, which are on the market now and are shown in Appendix B. A reliable FR determination is possible with greater than 5 percent by weight of FR, while for some polymers even an amount of 3 percent by weight is detectable (Bruker, 2009).



Hit No.		Color	Hit Quality	Compound Name	CAS number	Molecular formula	Molecular weight
1	☑	🟦	985	Acrylonitrile Butadiene Styrene (ABS)			
2	☐	🟪	938	Acrylonitrile Butadiene Styrene (ABS)			
3	☐	🟩	874	Acrylonitrile Butadiene Styrene (ABS)			

	Color		Path	Type
☑	🟥	049_4_2_1_L.0	C:\IR-Spektren\1_plastics	Query Spectrum

Figure 16: Example of result of a FTIR analysis with the use of OPUS/SEARCH, indicating ABS.



Result of IDENT evaluation:

Sample name: 049_5_3_1_L
Spectrum file: 049_5_3_1_L.0
File path: C:\IR-Spektren\1_plastics
Date and time (measurement): 04/02/2016 16:05:52.010 (GMT+1)
Method file: PolymerFlameRetardants_Analysis.FAA
File path: C:\Users\Public\Documents\Bruker\OPUS_7.5.18\IDENT

Group Name: PS 00, Hit qual.: 0.09

Sample is identified as PS 00

Result of IDENT evaluation:

Sample name: 049_5_4_1_L
Spectrum file: 049_5_4_1_L.0
File path: C:\IR-Spektren\1_plastics
Date and time (measurement): 04/02/2016 16:31:36.930 (GMT+1)
Method file: PolymerFlameRetardants_Analysis.FAA
File path: C:\Users\Public\Documents\Bruker\OPUS_7.5.18\IDENT

Group Name: ABS, 20% Chlorinated parrafins + 5% Sb2O3, 01, Hit qual.: 0.44

No unique identification .
No sufficient contact between sample and ATR crystal or polymer not in library.

Figure 17: Example of screened results by IDENT, where (a) the sample is identified as PS, (b) the sample could not be identified

3.2 Results and discussion

In this chapter the results of the experimental part of the thesis are presented and discussed. The results of the identification of polymers' types found in microwave ovens and personal computers are shown in Chapter 3.2.1.1 and Chapter 3.2.1.2 respectively. In Chapter 3.2.2 the results of the identification of flame retardants are discussed, followed by the comparison of the results with the literature data (Chapter 3.2.3) and the evaluation of FTIR as to whether it is a suitable method for the identification of polymers originating from WEEE (Chapter 3.2.4.1). Finally, in Chapter 3.2.4.2 the likelihood of microwave ovens and personal computers to contain FRs according to the findings of this thesis and previous work is discussed. The overall results, considering both identification of polymers and FRs, are presented in detail in Appendix C to Appendix F.

3.2.1 Identification of polymers

As mentioned in Chapter 3.1.4, besides FTIR, for the analysis of the samples, NIR, SSS and XRF were used, in order to obtain reference measurements aiming to evaluate the FTIR results. Considering the reference methods, for the purpose of identification of polymers' types, NIR and SSS are relevant.

3.2.1.1 Microwave ovens

Figure 18 shows the proportions of different polymer types as identified in microwave ovens' plastic housings, by the use of FTIR (OPUS/SEARCH and IDENT), NIR and SSS, as well as on the marks found on the plastic housings.

According to the results of the study, 25% of the microwave ovens' plastic housings were not labeled with regard to the polymer used. The remaining samples carried ABS (33.3%), PP (33.3%) and PC/ABS blend (8.3%) marks.

With the use of FTIR-OPUS/SEARCH and SSS it was possible to identify all polymers, while with FTIR-IDENT and NIR, 33.3% and 25% of the measurements respectively could not be identified. FTIR-IDENT was not able to identify the polymer type, when the contact of the device with the sample was not sufficient, due to the physical properties of the samples. 25% of the samples could not be identified by NIR, because of their black or very dark colour.

As seen in Figure 18 the most abundant polymer type is ABS, followed by PP, PC/ABS blend and PBT. As mentioned in Chapter 2.2.2 the composition of microwave ovens' plastic has not been extensively investigated in the past, thus no sufficient literature data exist about the polymer types used in the manufacture of this type of equipment. However, the high percentages of ABS and PP are accordant with reports regarding sWEEE polymers of Martinho et al. (2012) and Wäger et al. (2009) mentioned in Chapter 2.2.2. Moreover, Beigbeder et al. (2013), who investigated the nature of polymers from household appliances with the use of NIR technique, also report the abundance of ABS, followed by HIPS and PP.

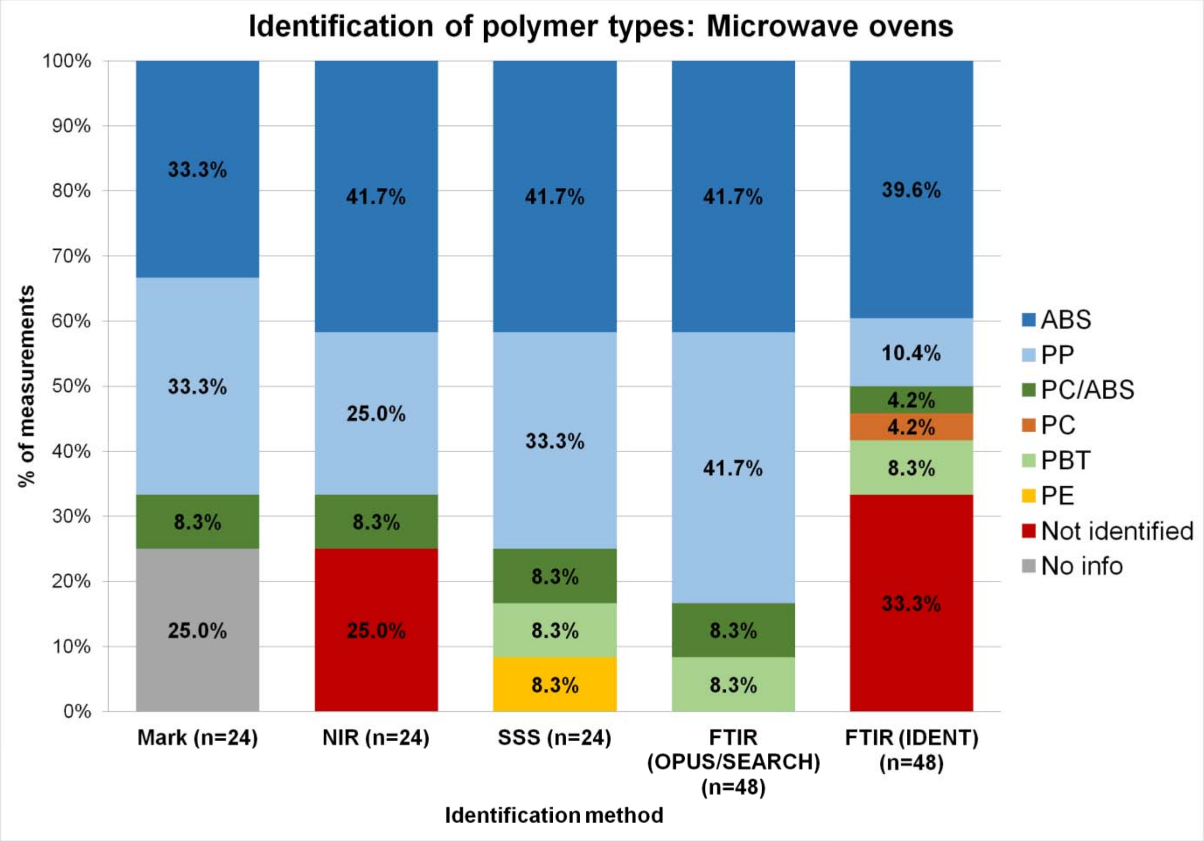


Figure 18: Results of identification of polymer types in microwave ovens' samples (n: number of measurements).

With the use of FTIR-OPUS/SEARCH all existing marks were verified, while the FTIR-IDENT verified all marks except for two cases, in which the one of the two measurements of the same sample showed PC/ABS blend and the other pure PC, for a plastic part labelled as PC/ABS. In addition, the results of FTIR-OPUS/SEARCH were validated by the NIR results (for non-black samples) and by SSS results, aside from the case of a plastic housing of one equipment, which was identified as PP with FTIR-OPUS/SEARCH and PE with SSS, which nonetheless was marked as PP. Thus, it can be inferred, that this variation of FTIR showed very reliable results regarding the identification of polymer types. As far as the IDENT variation is concerned, despite the fact that the majority of results were verified by the marks and the reference methods, an important disadvantage of this method was the high percentage of the samples (1/3 of the samples), which were not identified.

As mentioned in Chapter 3.1.4 in order to further evaluate the performance of the FTIR techniques, each plastic sample was measured twice (one measurement in each side of the sample), in order to assess the reproducibility of each method, namely the percentage of samples, for which both measurements presented the same result. After comparing the results of both measurements, the reproducibility of the OPUS/SEARCH method was found to be 100%, presenting perfect accordance between each couple of respective measurements. For the calculation of the reproducibility of the IDENT method, considering the high percentage of unsuccessful identification measurements, the couples of measurements, in which at least one was able to identify a polymer type, were taken into account. The reproducibility was found to be only 66.7%, much lower than the respective value for the OPUS/SEARCH method. This was caused mainly because in many cases only the one side of sample could be identified and due to the fact that, in the samples identified by the other methods as PC/ABS, the IDENT method could not identify in both sides the two components of the blend, indicating in the one side only the presence of PC.

3.2.1.2 Personal computers

As far as personal computers are concerned, Figure 19 shows the share of each polymer type identified by FTIR (OPUS/SEARCH and IDENT), NIR and SSS analysis.

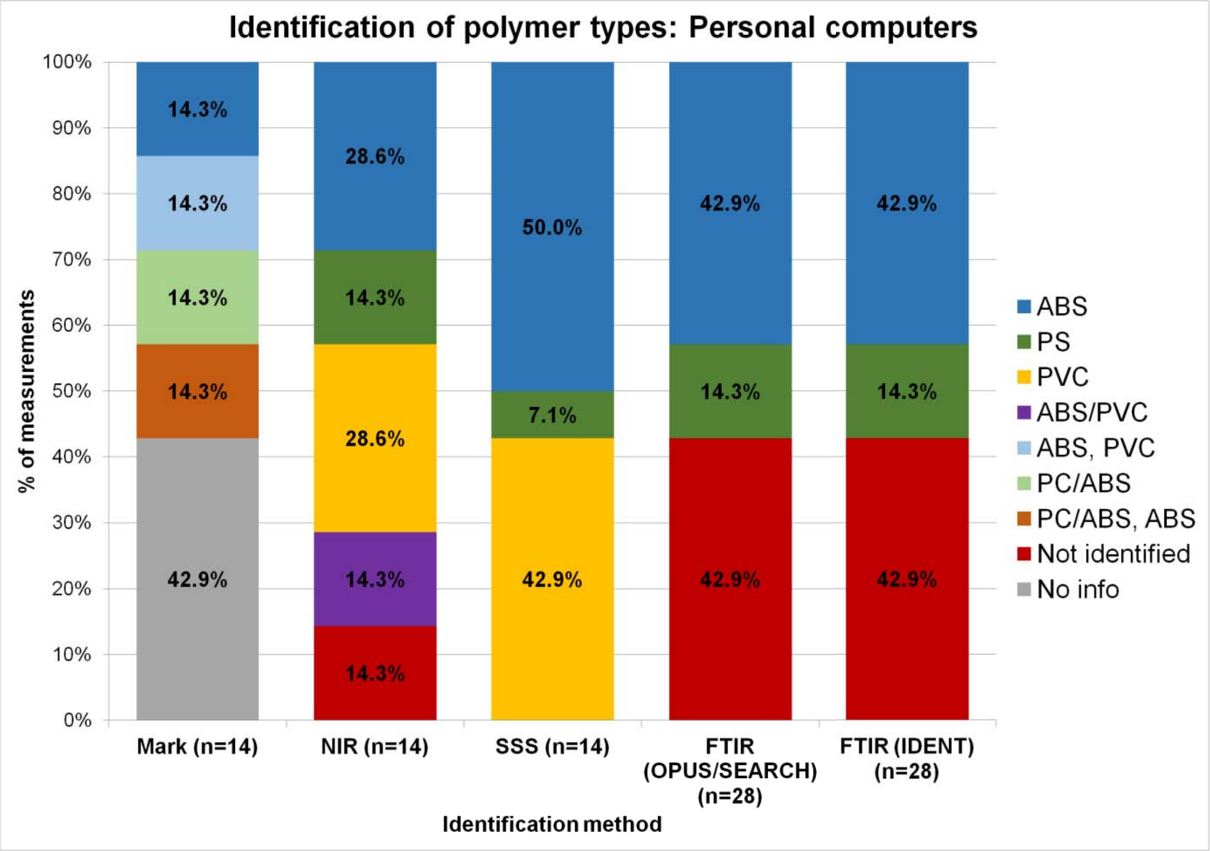


Figure 19: Results of identification of polymer types in personal computers' samples (n: number of measurements).

As seen in Figure 19, 42.9% of the samples carried no marks indicating the polymer type. The rest had marks with ABS, ABS in conjunction with PVC, ABS/PVC blend in conjunction with ABS and PC/ABS blend labels.

The OPUS/SEARCH method was not able to identify 42.9% of the samples, as the proposed reference spectra by the software had a low hit quality (247-717) and the results of the different measurements of the same sample were in none of the cases identical. The IDENT method could not identify the same samples as

OPUS/SEARCH. The incapability of the two methods to identify these samples can be related to the low intensity of the spectra obtained, due to the improper contact between the sample and the ATR device, which was caused because of the nature of the surface of the plastic samples. In all samples, which could not be identified, the XRF analysis found 31.1 wt.% - 41.1 wt.% chlorine, indicating PVC polymers. Additionally, these samples were identified by NIR and SSS as PVC or ABS/PVC blend, which suggests that there is a high possibility that FTIR encounters difficulties in the identification of PVC samples, probably because of a deficiency of PVC spectra variations in the reference libraries.

The rest of the samples were assigned to ABS (42.9%) and PS (14.3%) by both OPUS/SEARCH and IDENT methods, results which were verified by the other two methods, except for two samples, which were validated by NIR, but not by SSS. In this case the FTIR and NIR measurements indicated PS and the SSS indicated ABS, but it is highly possible that the result of SSS was unreliable due to the similar structure of the two types, as they both are styrene-containing polymers. Misidentifications between styrene-containing polymers using the SSS are also reported by Fanari (2016), who used this method to investigate plastic housing of vacuum cleaners and printers. The ABS labels found on the plastic housings were verified by the FTIR measurements and in the cases of labels indicating blends of two polymer types or the existence of two types, the one of the two polymers were identified, except of samples with label <ABS, PVC>, which could not be identified at all.

Additionally, the reproducibility of the two FTIR variants was calculated by comparing the results of identification of the two different sides of each sample. By excluding from the calculation the non-identified samples, the reproducibility of both OPUS/SEARCH and IDENT method was found equal to 100%.

Comparing the results of Figure 19 with the literature data mentioned in Chapter 2.2.2, the abundance of ABS found by all methods is also reported in the studies of Freegard et al. (2006), Reena et al. (2011) and Martinho et al. (2012). However, the high fraction of PVC found by NIR and SSS is not reported by the aforementioned studies, as it is considered as a polymer of secondary importance in the manufacture of personal computers (Freegard et al., 2006; Martinho et al., 2012; Reena et al., 2011; Wäger et al., 2010). Beigbeder et al. (2013) also examined the polymer types used in waste personal computers with the use of NIR technology and their results confirm that the most used polymer in the manufacture of personal computers is ABS, finding it in 40.3 wt.%, but also found an significant portion of PC/ABS (14.4 wt.%), which was not present in the results of FTIR analysis of this thesis. However, PC/ABS labels were found in 14.29% of the samples and labels of this blend along with pure ABS (<PC/ABS, ABS>) in the same portion (14.3%). Moreover, comparing the results of the study of Beigbeder et al. (2013), indicate a higher percentage of black polymers (31.2%) found in computer plastics, compared to the portion found in this thesis (14.3%).

3.2.2 Identification of flame retardants

Considering the methods applied for the reference measurements, SSS and XRF are relevant for the identification of some types of FRs, as they are able to detect and measure the concentration of inorganic elements present in the samples. As a result, these two methods can be used for the detection of bromine, the presence of which - over some specific concentrations- can be assigned to BFRs. A disadvantage of SSS and XRF is the fact that they are not able to identify the type of BFR compounds.

3.2.2.1 Microwave ovens

Table 9 shows the findings of the reference analysis of the microwave ovens' samples, investigating the bromine content of the plastics. Table 9 shows the portion of measurements, in which bromine was detected by the two methods, as well as the mean concentration and the range of concentrations of bromine found in the samples.

Table 9: Summary of the results of SSS and XRF reference analysis of microwave ovens' samples.

Identification method	% of samples in which bromine was detected	Mean bromine concentration (wt.%)	Range of concentrations of bromine detected (wt.%)	% of samples in which BFRs were detected
SSS	37.5	0.93	1.3 – 6.8	8
XRF	41.7	0.0024	0.002 – 0.013	0

The XRF method did not detect any bromine in 58.3% of the samples, while in the remaining 41.7% concentrations lower than 0.013 wt.% were found, indicating contamination of the recycling process and not the presence of BFRs, as it is too low to be an indication of the presence of BFRs. For BFRs to be effective, they are added in polymers in concentrations higher than 5 wt.%, which means that, considering the fact that the five most commonly use BFRs contain 59-83 wt.% bromine (Allae, 2003; Larssen et al., 1999), the bromine content in the samples should be higher than those found to indicate the presence of BFRs. As reported in the study of UNEP (2012), WEEE components, which originate from previous recycling of BFR-containing polymers, exhibit bromine contents in the range of 100-1000 ppm (0.01-0.1 wt.%), while Gallen et al. (2014) mentions that even a level of 10.000 ppm (1 wt.%) can be related to recycling of BFR-containing plastics. According to XRF analysis, 10 samples (41.7% of the samples) were found to have been contaminated with bromine probably through recycling.

The SSS method found low bromine contents (1.3-1.6%) in 29.2% of the samples. This amount is again considered to be related to contamination through recycling, because they are not significantly higher than the aforementioned limit of 1 wt.% set by Gallen et al. (2014), and they are still too low to achieve effective flame retardancy levels. In two samples (both originating from the same plastic housing) a bromine content of 6.8 wt.% and 6.1 wt.% was measured. The concentrations detected in those two measurements are high enough to be related to presence of BFRs, however, considering the higher precision of the XRF analysis and the fact that the XRF results indicated absence of bromine in those two samples, the reliability of those SSS results are in question.

As far as the FTIR analysis is concerned, on the one hand, the FTIR-OPUS/SEARCH method detected bromine-free FRs in 8.3% of the measurements, while the rest was found to be FR-free. This means, that this method did not find any BFRs in microwave ovens' samples, validating the XRF reference measurements. The identification of bromine-free FRs in some samples, indicated as FR 90 (not allocated, see Appendix B), is related to the presence of organophosphorus FRs, as the XRF and SSS measurements found 3.5-3.8 wt.% and 1.5 wt.% phosphorus respectively in the same samples. On the other hand, FTIR-IDENT detected BFRs in 37.5% of the measurements. The results of the FTIR-IDENT analysis are presented in Figure 20. The BFRs detected were HBCD, TBBPA, TBBPA bis(2,3-dibromopropyl ether) (TBBPA-DBPE) and TBBPA carbonate oligomer and were found in conjunction with ABS, PC/ABS, PP and PC respectively. Due to the incapability to match the obtained spectra with reference spectra, 33.3% of the measurements did not show any results, while the remaining FR–free samples were assigned to pure ABS (71%) and PBT (29%). The discrepancy between the FTIR-IDENT results and those of the reference methods, in combination with the incapability of this method to present results for 1/3 of the samples, leads to the conclusion that the FTIR-IDENT did not meet high levels of reliability.

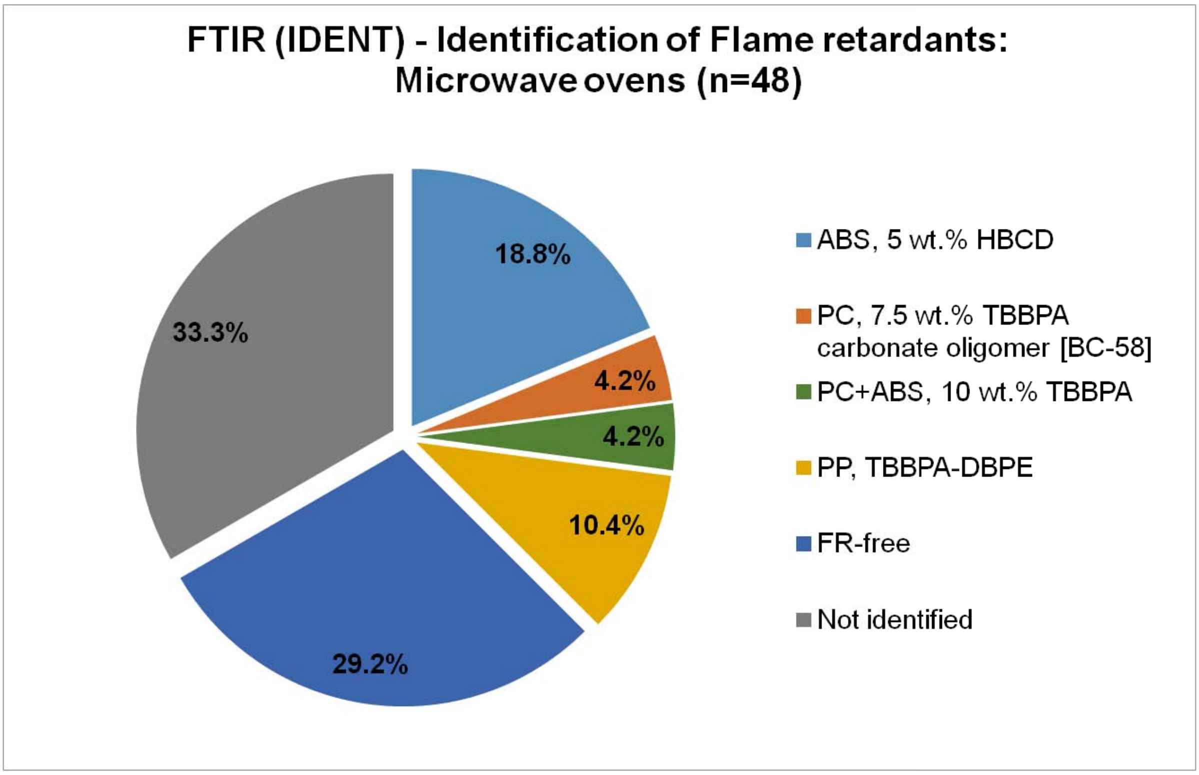


Figure 20: Results of FTIR (IDENT) analysis of microwave ovens' samples (n: number of measurements).

Moreover, the reproducibility of OPUS/SEARCH and IDENT was calculated, regarding both identification of polymers and flame retardants, meaning that a measurement was considered to be reproduced, if the second measurement of the same sample presented the exact same result for polymer and FR type detected. For

OPUS/SEARCH the reproducibility was 100%, as found in the case of polymer identification, while the IDENT method presented only 50% reproducibility. The percentage is lower than the respective for the polymer identification, due to the fact that in many cases the one side of the sample was identified as ABS and the other as ABS+5% HBCD, reducing the reliability of the indication of presence of the BFR.

3.2.2.2 Personal computers

Table 10 shows the percentage of SSS and XRF measurements of personal computers’ samples, in which bromine was detected. Table 10 also includes the mean concentration and the range of concentrations of bromine detected by the reference measurements.

Table 10: Summary of the results of SSS and XRF reference analysis of personal computers‘ samples.

Identification method	% of samples in which bromine was detected	Mean bromine concentration (wt.%)	Range of concentrations of bromine detected (wt.%)	% of samples in which BFRs were detected
SSS	0	0	0	0
XRF	35.7	0.0008	0.001 – 0.004	0

Using the SSS method, no bromine was detected in any of the measurements, while XRF found bromine in 35.7% of the samples, but in concentrations in a range of 0.001-0.004 wt.%, indicating, according to the limits of UNEP (2012) and Gallen et al. (2014) mentioned in Chapter 3.2.2.1, contamination during recycling and not the presence of BFRs.

During the FTIR analysis, 42.9% of the measurements, using both the OPUS/SEARCH and the IDENT method, could not obtain any results, probably due to the improper contact achieved during the measurement of PVC or PVC-containing samples. The measurement of the remaining samples using the OPUS/SEARCH did not detect any FRs and, are thus validated by the reference measurements, while 42.9% of the IDENT measurements identified ABS containing 5 wt.% HBCD. The remaining 14.3% of the samples were identified as BFR-free PS. The results of the IDENT method are illustrated in Figure 21.

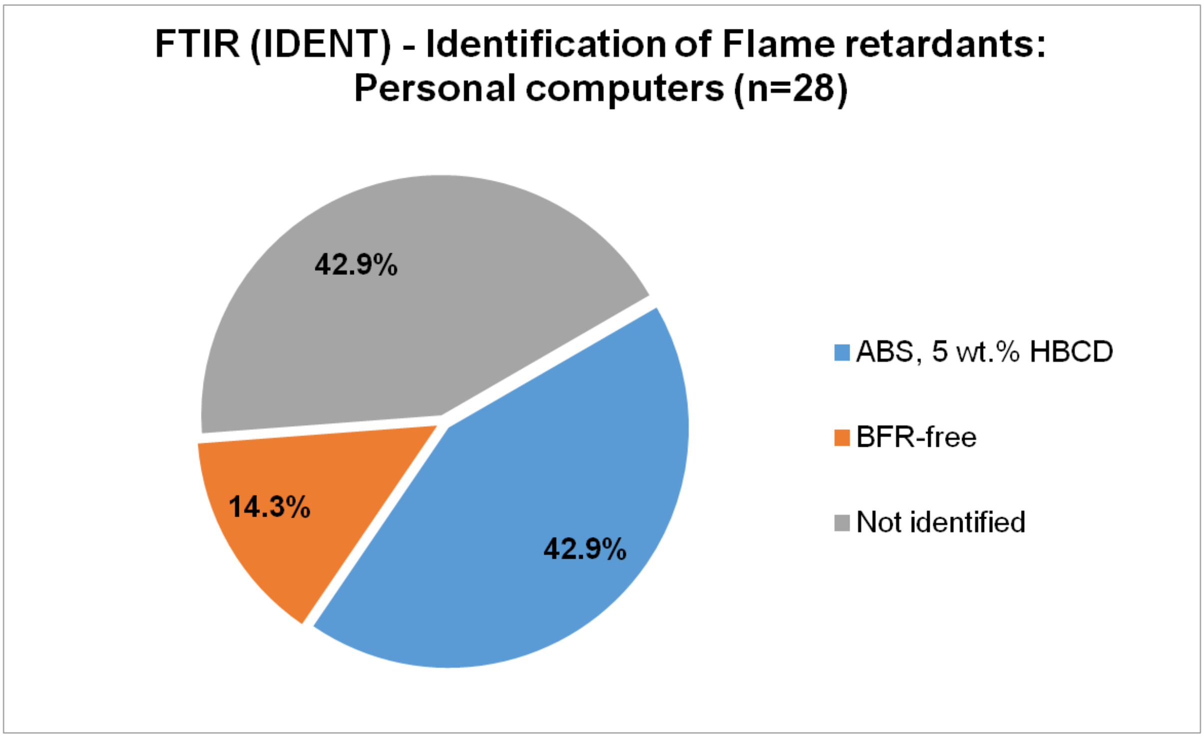


Figure 21: Results of FTIR (IDENT) analysis of personal computers' samples (n: number of measurements).

Despite the fact, that the IDENT method detected HBCD in a high portion, while the other methods did not find any BFRs, the reproducibility of this method was 100%, equal to the respective value achieved by OPUS/SEARCH. However, as seen also in Section 3.2.2.1, the IDENT method presented results, which were not validated not only by the reference analysis, but also by the OPUS/SEARCH method, in which the analysis can be done manually, having a better overview of the measured and reference spectra. For those reasons the IDENT method's result, regarding the identification of FRs, was considered unreliable.

An overview of all results concerning identification of both polymer types and flame retardants in microwave ovens and personal computers is presented on Table 11.

Table 11: Overview of the results of the experimental part of this thesis.

Identification method / **Equipment type**	**FTIR (OPUS/SEARCH)** (2 measurements/sample)	**FTIR (IDENT)** (2 measurements/sample)	**NIR** (1 measurement/sample)	**SSS** (1 measurement/sample)		**XRF** (1 measurement/sample)
Microwave ovens (12 devices, 24 samples)	ABS (41.7%), PP (27.1%), PP+EPDM (14.6%), PC/ABS + FR 90 (bromine free) (8.3%), PBT (8.3%)	ABS (20.8%), ABS + 5 wt.% HBCD (18.8%), PBT (8.3%), PP + TBBPA-DBPE (10.4%), PC/ABS + 10 wt.% TBBA (4.2%), PC + 7.5 wt.% Tribromophenyl terminated TBBA carbonate oligomer (4.2%), N.I. (33.3%)	ABS (41.7%), PP (25%), PC/ABS (8.3%), N.I. (25%)	ABS (41.7%), PP (33.3%), PC/ABS (8.3%), PBT (8.3%), PE (8.3%)	Bromine (37.5%), BFR (8.3%), Bromine-free (62.5%)	Bromine (41.7%), BFR (0%), Bromine-free (58.3%)
Personal Computers (7 devices, 14 samples)	ABS (42.9%), PS (14.3%), N.I. (42.9%)	ABS + 5 wt.% HBCD (42.9%), PS (14.3%), N.I. (42.9%)	ABS (28.6%), PS (14.3%), PVC (28.6%), ABS/PVC (14.3%), N.I. (14.3%)	ABS (50%), PS (7.1%), PVC (42.9%)	Bromine (0%), BFR (0%), Bromine-free (100%)	Bromine (35.7%), BFR (0%), Bromine-free (64.3%)

3.2.3 Comparison with previous work and additional reference analysis

Fanari's (2016) study titled "Identification of polymers and flame retardants in sWEEE: vacuum cleaners and printers." was carried out at the same institute as this thesis (Institute of Waste Management of the University of Natural Resources and Life Sciences, Vienna) and investigated the polymer and FR identification performance of FTIR using the same methodology on plastic housings of waste vacuum cleaner and printers. Fanari (2016), after applying the same sample preparation as described in this thesis, classified the samples into three groups, vacuum cleaners (32 samples), inkjet printers (18 samples) and multifunctional printers (45 samples). In this chapter, the results of Fanari's (2016) study are presented, as they are very useful, in order to have a better overview of the performance of this technique in polymer and FRs identification and further validate the conclusions extracted in previous chapters. Additionally, as Fanari (2016) did not apply XRF as a reference method, within the framework of this thesis, some XRF measurements using Fanari's (2016) samples were carried out in order to validate her results and check the reliability of the results of FTIR analysis.

Regarding the polymer types' identification of vacuum cleaners' plastic housings, OPUS/SEARCH's results showed good reliability, 100% confirmed by the SSS. On the contrary, the IDENT method did not identify 31.2% of the measurements, being unable to identify PP samples and showing correctly ABS, but in combination with HBCD, the presence of which was not verified by the reference and OPUS/SEARCH methods. Considering inkjet printers, OPUS/SEARCH exhibited a high level of reliability for polymer identification, confirming 81% of the moulding marks. In this case IDENT was able to identify all samples, but in many cases misidentifications between PS and HIPS occurred. Finally, as far as the polymer types' identification in multifunctional printers is concerned, the OPUS/SEARCH results were mainly confirmed by the producers' marks, while only a small portion of measurements (6.7%) was not identified. The IDENT method, after measuring the multifunctional printers' samples, presented a low level of reproducibility and could not identify 46% of the measurements (Fanari, 2016).

As reported by Fanari (2016) the FTIR analysis of the vacuum cleaners' plastic using the OPUS/SEARCH method showed no presence of FRs in the total number of samples, while the IDENT method indicated ABS with 5 wt.% HBCD in 64.1% of the measurements. As far as inkjet printers' samples are concerned, the OPUS/SEARCH results showed that 15% of the measurements contained bromine-free FRs and that none contained BFRs. The IDENT method identified 5.6% PS with HBCD and 8.3% PS containing Decabromodiphenylethane (Fanari, 2016). Decabromodiphenylethane or DBDPE is a BFR usually used to replace decaBDE, given their structural similarities and their similar physico-chemical properties (Egebäck et al., 2012; Kierkegaard et al., 2004; Ricklund et al., 2010).

In order to further validate the FTIR results, regarding the BFR identification, described in Chapter 3.2.2, a series of XRF measurements were carried out, investigating a part of the samples used in the work of Fanari (2016). The vacuum cleaners and inkjet printers were investigated within the framework of this thesis using the XRF handheld analyzer.

All 32 vacuum cleaner samples and 10 (out of a total of 18) inkjet printer samples were analyzed with the use of the handheld XRF analyzer, without the need of any further sample preparation. Table 12 includes the portion of samples, in which bromine was detected. In vacuum cleaners, 9.4% of the samples were found to contain bromine and the respective percentage for inkjet printers was 20%. However, as seen in Table 12 the range of concentrations found in both equipment was lower than 0.048 wt.% indicating that the bromine presence cannot be an indicator of FRs' presence and probably is caused by contamination during the recycling processes.

An overview of the portion of measurements, which detected BFRs by the XRF analysis, as well as by the FTIR analysis, regarding BFRs, carried out by Fanari (2016) are presented in Table 13. As seen in the table, the results obtained by the OPUS/SEARCH method have been validated by the XRF analysis, as all samples considering both appliances have been found to be BFR-free. As far as the IDENT method is concerned, it found BFRs in 68.8% of the vacuum cleaners' measurements (considering devices, in which the BFRs were found at least in half of the measurements) and in 13.9 % of the inkjet printer measurements. However, as this indication was not confirmed by the other two methods in combination with the fact that the IDENT method could not identify 31.3 % of the vacuum cleaners' measurements, this result should not be considered as reliable in this case.

Table 12: Summary of the results XRF reference analysis of vacuum cleaners and inkjet printers.

Equipment type	% of samples in which bromine was detected	Mean bromine concentration (wt.%)	Range of concentrations of bromine detected (wt.%)	% of samples in which BFRs were detected
Vacuum cleaners	9.4	0.00025	0.001 – 0.004	0
Inkjet Printers	20	0.0092	0.044 – 0.048	0

Table 13: Percentage of samples in which BFRs were detected by Fanari (2016) and by XRF reference analysis.

Equipment type / Identification method	Vacuum cleaners	Inkjet Printers
	% of samples in which BFRs were detected	
FTIR (OPUS/ SEARCH)	0	0
FTIR (IDENT)	68.8	13.9
XRF	0	0

Consequently, taking into account the results of microwave ovens' and personal computers' investigation, the results of the reference XRF analysis on Fanari's (2016) samples, as well as those reported in the study of Fanari (2016), it can be deduced that the results of the two studies are in a complete accordance. Both studies show a high level of reliability of OPUS/SEARCH software, while the IDENT was found to show a high proportion of incapability to identify samples, and a high percentage of misidentified BFRs. All results of the XRF reference analysis, as well as the FTIR results of Fanari's (2016) work are shown in detail in Appendix G and Appendix H.

3.2.4 Final considerations about the experimental part

As pointed out in Chapter 1.1, the goal of this thesis was to provide information as to whether the FTIR technique is suitable and reliable for the identification of WEEE polymers and FRs, and whether the plastic housings of microwave ovens and personal computers are likely to contain FRs, in order to facilitate the recycling process of this kind of material. In Chapters 3.2.4.1 and 3.2.4.2 these two questions are answered according to the results obtained by the experimental part of this thesis.

3.2.4.1 Evaluation of FTIR for polymer and FRs identification

According to the evaluation of the results, it was obvious that during the FTIR measurements, different results were obtained using the two different identification software types (OPUS/SEARCH and IDENT). Thus, it can be inferred that the performance of the FTIR technique in the investigation of plastic samples is strongly dependent on the used software and library. For this reason, the performance of the OPUS/SEARCH and IDENT is separately evaluated in Chapters 3.2.4.1.1 and 3.2.4.1.2 respectively and in Chapter 3.2.4.1.3, some final considerations are pointed out about the FTIR method in general. The main advantages and disadvantages of the two identification software types, as found in the experimental part of this thesis, are presented in Table 14.

3.2.4.1.1 Evaluation of FTIR-OPUS/SEARCH

As far as the identification of polymer types is concerned, all of the OPUS-SEARCH method's results for microwave ovens' samples, with the exception of the samples originating from one plastic housing, were validated not only by the NIR and SSS reference analysis but also by the marks found on the plastic housings (if existent). In the case where the results were not completely validated, the OPUS/SEARCH identified the samples as PP, which was approved by the mark but not by the SSS (the samples were black, thus the NIR measurement was not possible), which identified them as PE. After careful analysis of the obtained FTIR spectra, it was concluded that even these results were reliable and the divergence with the reference results is probably a wrong indication by the SSS device. In personal computers' samples, the method was not able to identify the samples, which were found to contain high concentrations of chlorine, indication of pure PVC or PVC blends. This can be linked to the insufficient contact between the samples and the ATR crystal, caused by the roughness of the samples' surface or to a PVC spectra variations deficiency of the reference library. The rest of the personal computers' measurements were validated by the reference measurements and the labels, except of one discrepancy, where a polymer identified as ABS was labeled by the manufacturer as PC/ABS blend. This divergence, considering that the reference methods also indicated ABS, can be related to false information given in by the mark or abundance of ABS in the PC/ABS blend. Taking into account these results, and the perfect reproducibility achieved by this method in this experiment, the performance of this technique in the identification of polymer types achieved a very high reliability, with an exception of PVC samples.

Regarding the identification of FRs, OPUS/SEARCH's results were fully validated by the reference measurements, with an exception of two measurements of SSS, which detected 6.1 and 6.8 wt.% bromine, while the OPUS/SEARCH analysis did not detect any BFR. However, as this SSS result was not validated by the reliable XRF method, the OPUS/SEARCH result was considered as reliable too. This FTIR variant was also able to identify bromine-free FRs, the presence of which was validated by the XRF measurement, providing an extra advantage to this technique. As mentioned in Chapter 3.2.3, the good performance status of FTIR-OPUS/SEARCH was verified by the overview on Fanari's (2016) study, in which the same methodology was applied on different types of sWEEE.

A substantial advantage of the FTIR-OPUS/SEARCH method is the capability provided to the user, immediately after the measurement, to have access to the obtained and reference spectra and check the results, having the possibility to manipulate and correct the software's choices. This function, although making this technique more reliable, requires a higher level of expertise and increases the analysis time. This drawback, in conjunction with the -in some cases- higher sample preparation requirements, makes other methods such as NIR and XRF more attractive for automated sorting facilities.

3.2.4.1.2 Evaluation of FTIR-IDENT

Regarding the identification of polymer types, the IDENT software's results for ABS and PBT polymers, which constituted the 50% of the samples, have been validated by the reference methods and the marks, in cases, in which they were present. However, only 25% of the samples, indicated as PP by FTIR-OPUS/SEARCH, the reference methods and the labels, could be correctly identified. The remaining 75% could not be identified at all. The weak performance of IDENT in identification of PP is also reported by Fanari (2016). Additionally, a difficulty in identification of blends was observed, as PC/ABS blends were not always identified correctly, misclassifying the samples as PC in some cases. As far as the personal computers' investigation is concerned, the results were exactly the same as those given by the OPUS/SEARCH, presenting the incapability to identify samples made of PVC. However, the overall findings indicate an obvious weakness in terms of reliability compared with the OPUS/SEARCH method, regarding the polymer type identification.

The IDENT method detected BFRs in a significant proportion of microwave ovens' and personal computers' measurements, results, which were not validated by neither SSS nor XRF analysis. These results, combined with the inability to identify a significant number of samples (33.3% for microwave ovens and 42.9% for personal computers) indicates a poor performance of this technique in the identification of FRs. This reasoning is also confirmed by the reference XRF analysis of the samples used in Fanari's (2016) work, which did not find bromine in significant amounts, while the IDENT method detected BFRs in 68.8% of the vacuum cleaners' samples and in 13.9 % of the inkjet printer samples (Fanari, 2016). Additionally, the IDENT method exhibited a poor reproducibility in the case of microwave ovens' investigation concerning both identification of polymers and FRs. Furthermore, a significant disadvantage of this method compared to the OPUS/SEARCH is the inability to access the reference spectra limiting the researcher's means to interpret the results and search for alternative and more suitable results in cases of misidentification. Finally, as the IDENT library includes only bromine-containing FRs (see Appendix B), the IDENT software is unsuitable for identification of bromine-free FRs.

Table 14: Advantages and disadvantages of OPUS-SEARCH and IDENT as found in this thesis.

	FTIR - OPUS/SEARCH	**FTIR - IDENT**
Advantages	• High reliability • High levels of reproducibility • Access to obtained and reference spectra for further manual analysis • Identification of bromine-free FRs	• Automatical and fast identification • Not high level expertise required
Disadvantages	• High level of expertise required • Not suited for automated sorting processes	• Low reliability • Low reproducibility • High portion of samples could not be identified • Unsuitable for identification of bromine-free FRs

3.2.4.1.3 Final considerations about the FTIR technique

Taking into account the results of the FTIR analysis of this thesis, as well as the conclusions extracted by Fanari's (2016) work, it can be construed that the performance of this technique is dependent on the software and library used for the identification. On the one hand, the OPUS/SEARCH showed satisfying results, considering the identification of both polymer types and FRs, with an exception of the identification of PVC polymers. On the other hand, the IDENT method presented in several cases results indicating the presence of FRs, which was in no case validated by the reference methods. Moreover, this method showed in a significant number of cases inability to identify both polymer types and FRs. The significantly better performance of OPUS/SEARCH is also depicted on the better reproducibility achieved by this method in identification of both polymers and FRs, compared to the respective value of the IDENT method.

A difference between those two variants of FTIR methods, which makes the OPUS/SEARCH more advantageous, is the possibility offered, immediately after the measurement, to have access to the reference spectra, which are used of the software to identify the polymers. This provides the ability to evaluate the result and compare with other possible spectra, which could be more relevant than the proposed by the software spectrum. The possibility to manually evaluate the result given by the OPUS/SEARCH is also not provided by the other reference techniques used in this thesis, namely by the mIRoSpark and xSORT handheld XRF analyzer, which makes the OPUS/SEARCH method more advantageous in this scope.

Another factor, which led to more reliable results by the OPUS/SEARCH method compared to those of IDENT, is the better performance of the BPAD library and IR - Flame Retardants - Bio-Rad Sadtler IR Spectra Database used by OPUS/SEARCH than the library used by IDENT. The former libraries exhibit also the advantage of including bromine-free FRs, in contrast to the IDENT library, which includes only BFRs (see Appendix B). Thus, it is safe to assume that the performance of identification by FTIR can be significantly influenced by the used library leading to the conclusion that further development of polymer and FR libraries is essential in order to achieve even higher levels of reliability, by avoiding misidentifications (as was the case for example with PVC samples), and better separation of FR-containing plastics.

Comparing the FTIR technique in general with the reference methods used in this experiment, a strength observed relative to the NIR technique, is the capability to identify black samples. This is crucial, because black or dark coloured plastic parts make up a considerable fraction of the overall e-waste plastic stream. Specifically, the analysis of this thesis found black samples to represent the 25% of the microwave ovens' samples and 14.3% of the personal computer' samples.

Regarding the identification of FRs, an important advantage of the FTIR method in comparison with the SSS and XRF, which were used as reference methods, is the ability to identify the BFR compounds contained in the analyzed samples. Contrariwise, the other two methods are only able to detect and quantify bromine as an indication of the presence of BFRs. This makes them suitable only for a screening as to whether samples contain BFRs but not for further research purposes. For this reason, and taking into account that it can simultaneously identify the polymer type, the FTIR technique can be considered as a more complete method for the investigation of WEEE plastics.

However, there are also some disadvantages of the FTIR technique found during the experimental procedure. The possibility to manually evaluate the result given by the OPUS/SEARCH requires a higher level of user's expertise, making it a very useful tool for research, but unsuitable for application in automated sorting systems, for example in dismantling or recycling plants. To the contrary, other techniques, such as those used as reference methods, although they barren of the possibility of immediate access to the obtained and reference spectra, are usually used for research or industrial purposes, because of the extremely fast screening procedure they offer, making them, for instance, a very relevant option for a fast screening regarding BFRs in recycling facilities.

Another drawback of the FTIR technique using ATR module is the requirements related to the sample preparation. As the contact with the device must be very good in order to obtain a reliable spectrum, the sample must be flat. To achieve this in this thesis, it was necessary in some cases to cut the plastic parts into very small pieces, which required physical strength and was quite time consuming. In this view, the NIR, SSS and XRF equipment used within the framework of this study were more advantageous, as they required less or even none sample preparation. Furthermore, the xSORT XRF handheld analyzer, being portable, offered a much easier analysis more fitted for industrial purposes than the FTIR-ATR analysis. The use of portable FTIR equipment or devices using other scanning modules instead of the ATR, such as diffuse or contactless reflection modules, can help overcome this kind of drawbacks. However the capability to achieve the precision and reliability levels of ATR is still in question.

Table 15 summarizes the main advantages and disadvantages of the FTIR-ATR technique according to the results of the experimental procedure, compared to the reference methods used

Table 15: Advantages and disadvantages of FTIR-ATR technique compared to the reference methods used in this thesis.

	FTIR - ATR
Advantages	• Identification of both polymer types and FRs • Access to obtained and reference spectra for further manual analysis • Identification of the type of BFR compound • Identification of bromine-free FRs • Investigation of black samples
Disadvantages	• More sample preparation required • Higher level of expertise required • Not portable • Not suited for automated sorting processes

3.2.4.2 Presence of FRs in microwave ovens and personal computers

Besides evaluation of FTIR as an identification technique for polymers and FRs, this thesis' experimental part aimed to draw a conclusion as to whether microwave ovens' and personal computers' plastic housings are likely to contain FRs or not. By providing this information, this thesis aspires to contribute to the creation of a database, regarding the probability of presence of FRs in each WEEE, which could be useful for dismantling processes and lead to higher quality of recycling products.

According to the results of the experiments, all methods, except for the FTIR-IDENT, proved the absence of BFRs, the type of FRs subjected to the EU regulations, in all microwave ovens' samples investigated. Only in 8.3% of the measurements, which concerned samples originating from only one plastic housing, bromine-free FRs were found by the FTIR-OPUS/SEARCH analysis. As far as personal computers are concerned, none of the methods applied found any FRs. Thus, the results of this thesis suggest that both microwave ovens' and personal computers' plastic housings are not likely to contain FRs.

On the one hand, the results concerning microwave ovens is in accordance with the reports of French Ministry of Ecology, Sustainable Development and Energy (2012) and Novak (2001), according to which microwave ovens, as well as most of the household EEE, are not likely to contain FRs. On the other hand, most previous works investigating personal computers reported a quite high possibility to find FRs, and especially BFRs, in this type of equipment (Chen et al., 2012; Reena et al., 2011; Wäger et al., 2010), which was not validated by the results of this thesis.

Table 16 presents results of several studies investigating FRs in personal computers using the XRF technique. The average concentration of bromine found in personal computer's samples by the XRF analysis of this thesis was 0.0008 wt.%, significantly lower than those found in the studies of Taurino et al. (2010), Aldrian et al. (2015) and Morf et al. (2005) (see Table 16). The mean concentrations found in these studies are an indication of presence of BFRs in a portion of the examined samples. Aldrian et al. (2015) found in 39% of the 1598 monitor housings they used, over 5 wt.% bromine. However, the study of Gallen et al (2014) did not find significant presence of BFRs in personal computers' plastics. Gallen et al. (2014), who measured 119 plastic samples originating from personal computers using XRF, detected bromine in concentrations higher than 1 wt.% only in 3% of the samples, meaning that the portion which contained BFRs might be even lower, as the presence of BFRs is indicated by concentrations exceeding approximately 3 wt.%. Because of this divergence observed between the findings of different studies considering personal computers, it is highly recommended that future work should further examine this kind of equipment.

A factor which led to so low bromine concentrations in the results of this thesis is that almost 43% of the samples were found to be made of PVC or PVC blends, in which, according to Wäger et al. (2010), BFRs are only scarcely applied. This high proportion of PVC is not in accordance with reports of previous works, as it is considered as a polymer of secondary importance in the manufacture of personal computers (Freegard et al., 2006; Martinho et al., 2012; Reena et al., 2011; Wäger et al., 2010). This deviation of the results, combined with the fact that the mean concentrations of bromine shown in Table 16 significantly diverge from those of this thesis, in which no BFRs were detected, introduces uncertainty concerning the representativeness of the fraction of personal computers' plastic housings used in the experiment, regarding the presence of BFRs.

The results of the XRF measurements of this thesis suggest that 39.5 % of the samples are contaminated with bromine originating by the recycling of BFR-containing plastics. This quite high percentage is in agreement with the findings of the studies of Aldrian et al. (2015) and Gallen et al. (2014). Aldrian et al. (2015) found less than 0.9 wt.% concentration of bromine in 58.9% of the housings they examined, indicating contamination from recycled BFR-containing plastics. Gallen et al. (2014), analyzing personal computers' plastic, detected bromine in 45 % of the samples, but its existence in 42% of the cases was a result of recycling contamination.

Table 16: Results of past studies investigating the bromine content in personal computers' plastic samples.

Study	Identification Technique	Investigated equipment	Samples used	Results (mean Concentration)
Taurino et al., 2010	XRF	Personal computers	5 measurements of a mix of several crashed computers' polymers	4.39 wt.% Bromine
Aldrian et al., 2015	XRF	Personal computer monitor housing	1598 Samples	3.2 wt.% Bromine
Morf et al., 2005	XRF	TV/Personal computer housings	4 samples, each originating from homogenization of 20kg of plastic housings	4.4 ± 0.2 wt.% Bromine

The high portion of contaminated polymers with bromine used in the manufacture of WEEE, although not caused by direct application of BFRs, is an issue which should raise awareness, as bromine keeps being "trapped" in the recycling loop. The concentrations found in several samples in the studies of Aldrian et al. (2015) and Gallen et al. (2014) are often exceeding the permitted level of 1000 ppm for PBB and PBDE set by the RoHS Directive. Thus, future work should not only focus on the detection of BFRs in WEEE, but also on the examination of the contamination caused by the recycling of those substances.

Finally, in order to contribute to the purpose of this thesis and Fanari's (2016) study, namely the creation of a database, including information about the likelihood for BFRs to be present in different types of sWEEE and WEEE in general, future works should also investigate other types of WEEE as to their BFR content. Of crucial importance is the investigation of equipment types, for which only limited data exist, as was the case with microwave ovens.

4. CONCLUSIONS

The growing amount of WEEE in conjunction with their hazardous content has raised awareness during the last decades among the administrative and scientific community. As a result, a group of hazardous substances, the FRs, contained in a significant fraction of e-waste have been subject not only of a high number of scientific studies, but also of several EU regulations, restricting the use of several FRs and regulating their treatment.

One of the requirements of the EU regulations, concerning FRs, is the separation of WEEE plastic containing some BFR compounds before recycling. Thus, the development of effective techniques for the identification of FRs in e-waste plastic is necessary, in order to comply with the regulation and produce "clean" secondary material. Of significant importance is also the proper identification and separation of different polymer types aiming to increase the quality of the WEEE recycling product. To these purposes, an experiment was planned, investigating plastic housings of microwave ovens and personal computers by the use of FTIR and aiming to evaluate this technique in the identification of polymers and FRs. The measurements were carried out by a FTIR-ATR equipment and for the identification, two different software with different polymer and FRs libraries were used, namely the OPUS/SEARCH and the IDENT method. Additionally, NIR, SSS and XRF were applied as reference methods, in order to validate the FTIR results.

Regarding the identification of polymer types, the OPUS/SEARCH had a very satisfying performance, with an exception considering PVC samples, while the IDENT method was not able to identify a significant portion of samples, showing a poor performance. As far as the identification of FRs is concerned, the OPUS/SEARCH found FRs only in 8.3% of the samples and no BFRs at all, results, which were validated by the reference methods. The IDENT method, on the other hand, detected BFRs in a significant amount of measurements, which were not verified by the SSS and XRF results, which leads to the inference that the used library is not sufficient for the effective separation of BFR-containing plastics.

The aforementioned results indicate that the FTIR technique can be valuable for the purpose of separation of polymers, but its performance strongly depends on the used software and library. An advantage of the OPUS/SEARCH method compared with the IDENT method and the reference methods used is the indication of the obtained and reference spectra of the library immediately after the measurement. This provides the additional option to manually evaluate the proposed results. However, this procedure requires a high level of expertise of the user, making this technique more suitable for research purposes, while its suitability for automated sorting systems is doubted, considering the extremely fast scanning procedure offered by other tested methods, such as handheld XRF devices.

Furthermore, the verified OPUS/SEARCH results of the analysis suggest that both microwave ovens and personal computers are not likely to contain FRs, information which can be used to help boosting the recycling process by making easier the recognition of FR-plastics. This inference is confirming several previous studies, considering microwave ovens (French Ministry of Ecology, Sustainable Development and Energy, 2012; Novak, 2001), but not the majority of previous work about personal computers, which report a significant FR-plastic fraction in this kind of equipment (Aldrian et al., 2015; Chen et al., 2012; Morf et al., 2005; Taurino et al., 2010).

For this reason, the investigation of personal computers, as well of other types of WEEE, should be continued in future studies, aiming to contribute to the creation of a database containing lists of equipment which are more likely or not to contain FRs. This database can provide useful information to dismantling and recycling facilities, which can lead to a better separation of FR-containing plastics and an increase of the recycling efficiency. The findings of this thesis also provide some useful indications about the performance of FTIR in the identification of polymers and FRs, but there is a need to further investigate in this direction using not only polymers originating from other types of equipment, but also other identification techniques.

Finally, the results of the XRF and SSS reference analysis, as well as results of other studies, suggest, that a significant fraction of WEEE plastics is contaminated with bromine, originating from the recycling of BFR-containing polymers. These contaminated polymers often contain bromine concentrations higher than 0.1 wt.%, which, although not related with direct use of BFRs, exceed the allowed level for PBB and PBDE set by the RoHS Directive. Thus, future work should also focus on this issue, in order to avoid "trapping" of bromine in the recycling loop aiming to avoid the negative environmental and health impacts related to them.

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Appendices

Appendix A: Code numbers for Flame Retardants according to DIN EN ISO 1043-4, Plastics – Symbols and abbreviated terms, Part 4: Flame retardants

Code numbers for flame retardants	
Code numbers are grouped according to the chemical composition of the flame retardant.	
HALOGONATED COMPOUNDS	
Code	
10	aliphatic/alicyclic chlorinated compounds
11	aliphatic/alicyclic chlorinated compounds in combination with antimony compounds
12	aromatic chlorinated compounds
13	aromatic chlorinated compounds in combination with antimony compounds
14	aliphatic/alicyclic brominated compounds
15	aliphatic/alicyclic brominated compounds in combination with antimony compounds
16	aromatic brominated compounds (excluding brominated diphenyl ether and biphenyls)
17	aromatic brominated compounds (excluding brominated diphenyl ether and biphenyls) in combination with antimony compounds
18	polybrominated diphenyl ether
19	polybrominated diphenyl ether in combination with antimony compounds
20	polybrominated biphenyls
21	polybrominated biphenyls in combination with antimony compounds
22	aliphatic/alicyclic chlorinated and brominated compounds
23, 24	not allocated
25	aliphatic fluorinated compounds
26 to 29	not allocated
NITROGEN COMPOUNDS	
30	nitrogen compounds (confined to melamine, melamine cyanurate, urea)
31 to 39	not allocated
ORGANIC PHOSPHORUS COMPOUNDS	
40	Halogen-free organic phosphorus compounds
41	Chlorinated organic phosphorus compounds
42	Brominated organic phosphorus compounds
43 to 49	Not allocated
INORGANIC PHOSPHORUS COMPOUNDS	
50	ammonium orthophosphates
51	ammonium polyphosphates
52	red phosphorus
53 to 59	not allocated
METAL OXIDES, METAL HYDROXIDES, METAL SALTS	
60	aluminum hydroxide

61	magnesium hydroxide
62	antimony (III) oxide
63	alkali-metal antimonite
64	magnesium/calcium carbonate hydrate
65 to 69	not allocated
BORON AND ZINC COMPOUNDS	
70	inorganic boron compounds
71	organic boron compounds
72	zinc borate
73	organic zinc borate
74	not allocated
SILICA COMPOUNDS	
75	inorganic silica compounds
76	organic silica compounds
77 to 79	not allocated
OTHERS	
80	Graphite
81 to 89	not allocated
90 to 99	not allocated

Appendix B: Polymer/FR-combinations included in the Bruker IDENT Database.

Flame Retardant	Polymer												
Decabromodiphenyl ether (DecaBDE)	PBT		ABS	PC+ABS	SB	PS	LDPE	PE	PP+EPDM	PP			PBT
Polybrominated diphenyl ether (PBDE)			ABS		SB	PS							
Decabromobiphenyl (DeBB)			ABS		SB	PS		PE		PP		PA6	
Tetrabromobisphenol-A (TBBPA)			ABS	PC+ABS									
TBBA-bis(2,3 dibrompropylether)	PBT						LDPE			PP			
TBBA Oligocarbonate	PBT					PS							PBT
Brominated oligo carbonate	PBT	PC										PA6	
Polybrominated polystyrene	PBT										PA66		PBT
Polydibromostyrene											PA66	PA6	
Hexabromcyclododecane (HBCD)			ABS		SB (HIPS)	PS							
Brominated aromatic Triazine													
Octabromodiphenylether (OctaBDE)			ABS			PS							
Ethylene-Bisphenol tetrabromopthalimide			ABS	PC+ABS		PS							PBT
Chlorinated paraffins			ABS		SB								
Epoxy oligomer with TBBPA			ABS		SB	PS							
Polybrominated Bisphenol-derivative										PP			
Brominated Triphenyl Indane			ABS										
Hexabromodiphenoxyethane			ABS			PS							
Tribromophenyl terminated TBBPA carbonate oligomer		PC											PBT

Appendix C: Results of identification of microwave oven samples by FTIR (OPUS/SEARCH and IDENT).

	FTIR (OPUS/SEARCH)		FTIR (IDENT	
Sample*	**1st measurement**	**2nd measurements**	**1st measurement**	**2nd measurements**
1.1	ABS	ABS	ABS 00	ABS 00
1.2	ABS	ABS	ABS 00	ABS 00
2.1	ABS	ABS	ABS 00	ABS; 5 wt.% HBCD
2.2	ABS	ABS	ABS; 5 wt.% HBCD	ABS 00
3.1	ABS	ABS	ABS; 5 wt.% HBCD	N.I.
3.2	ABS	ABS	ABS; 5 wt.% HBCD	ABS; 5 wt.% HBCD
4.1	ABS	ABS	ABS	ABS
4.2	ABS	ABS	ABS	ABS
5.1	ABS	ABS	ABS; 5 wt.% HBCD	ABS; 5 wt.% HBCD
5.2	ABS	ABS	ABS; 5 wt.% HBCD	ABS; 5 wt.% HBCD
6.1	PP	PP	N.I.***	N.I.
6.2	PP	PP	N.I.	N.I.
7.1	PBT	PBT	PBT	PBT
7.2	PBT	PBT	PBT	PBT
8.1	PP	PP	PP, PE-68****	PP, PE-68
8.2	PP	PP	N.I.	PP, PE-68
9.1	PP	PP	N.I.	N.I.
9.2	PP	PP	N.I.	N.I.
10.1	PC/ABS, FR 90	PC/ABS, FR 90	PC+ABS, 10 wt.% TBBPA	PC, 7.5 wt.% BC-58
10.2	PC/ABS, FR 90	PC/ABS, FR 90	PC, 7.5 wt.% BC-58*****	PC+ABS, 10 wt.% TBBPA
11.1	PP + EPDM**	PP + EPDM	N.I.	N.I.
11.2	PP + EPDM	PP	N.I.	N.I.
12.1	PP + EPDM	PP + EPDM	N.I.	PP, PE-68
12.2	PP + EPDM	PP + EPDM	N.I.	PP, PE-68

*Sample numbering: 1st number indicates the number of plastic housing and 2nd number indicates the number of sample, ** EPDM: Ethylene Propylene Diene Monomer, *** N.I.: Not Identified, **** PE-68: TBBA bis(2,3-dibromopropyl ether), ***** BC-58: Tribromophenyl terminated TBBA carbonate oligomer

Appendix D: Mark information and results of identification of microwave oven samples by NIR, SSS and XRF

Sample*	MARK	NIR	SSS	SSS (Bromine)	XRF (Bromine)
1.1	ABS	ABS	ABS	1.3 wt.%	0.003 wt.%
1.2	ABS	ABS	ABS	1.3 wt.%	0.003 wt.%
2.1	ABS	ABS	ABS	1.3 wt.%	0.013 wt.%
2.2	ABS	ABS	ABS	N.D.****	0.012 wt.%
3.1	no info**	ABS	ABS	N.D.	N.D.
3.2	no info	ABS	ABS	N.D.	N.D.
4.1	ABS	ABS	ABS	1.3 wt.%	N.D.
4.2	ABS	ABS	ABS	N.D.	N.D.
5.1	ABS	ABS	ABS	1.3 wt.%	N.D.
5.2	ABS	ABS	ABS	1.3 wt.%	N.D.
6.1	no info	N.I.***	PP	N.D.	0.002 wt.%
6.2	no info	N.I.	PP	N.D.	N.D.
7.1	no info	N.I.	PBT	N.D.	0.01 wt.%
7.2	no info	N.I.	PBT	N.D.	0.008 wt.%
8.1	PP	N.I.	PE	N.D.	N.D.
8.2	PP	N.I.	PE	N.D.	N.D.
9.1	PP	PP	PP	6.8 wt.%	N.D.
9.2	PP	PP	PP	6.1 wt.%	N.D.
10.1	PC/ ABS	PC/ABS	PC/ABS	N.D.	0.002 wt.%
10.2	PC/ ABS	PC/ABS	PC/ABS	1.6 wt.%	0.002 wt.%
11.1	PP-MD20	PP	PP	N.D.	N.D.
11.2	PP-MD20	PP	PP	N.D.	0.003 wt.%
12.1	PP-MD20	PP	PP	N.D.	N.D.
12.2	PP-MD20	PP	PP	N.D.	N.D.

*Sample numbering: 1st number indicates the number of plastic housing and 2nd number indicates the number of sample, **no info: No mark found, ***N.I.: Not Identified, ****N.D.: Not Detected

Appendix E: Results of identification of personal computer samples by FTIR (OPUS/SEARCH and IDENT).

	FTIR (OPUS/SEARCH)		FTIR (IDENT)	
Sample*	**1st measurement**	**2nd measurement**	**1st measurement**	**2nd measurement**
1.1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD
1.2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD
2.1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD
2.2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD
3.1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD
3.2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD
4.1	PS	PS	PS	PS
4.2	PS	PS	PS	PS
5.1	N.I.**	N.I.	N.I.	N.I.
5.2	N.I.	N.I.	N.I.	N.I.
6.1	N.I.	N.I.	N.I.	N.I.
6.2	N.I.	N.I.	N.I.	N.I.
7.1	N.I.	N.I.	N.I.	N.I.
7.2	N.I.	N.I.	N.I.	N.I.

*Sample numbering: 1st number indicates the number of plastic housing and 2nd number indicates the number of sample, **N.I.: Not Identified

Appendix F: Mark information and results of identification of personal computer samples by NIR, SSS and XRF

Sample*	MARK	NIR	SSS	SSS (Bromine %)	XRF (Bromine %)
1.1	ABS	N.I.	PS	N.D.***	0.004 wt.%
1.2	ABS	N.I.	ABS	N.D.	0.004 wt.%
2.1	PC+ABS-FR(40)	ABS	ABS	N.D.	N.D.
2.2	PC+ABS-FR(40)	ABS	ABS	N.D.	N.D.
3.1	ABS, PC+ABS-FR(40)	ABS	ABS	N.D.	N.D.
3.2	ABS, PC+ABS-FR(40)	ABS	ABS	N.D.	N.D.
4.1	no info**	PS	ABS	N.D.	N.D.
4.2	no info	PS	ABS	N.D.	N.D.
5.1	ABS-FR, PVC	ABS/PVC	PVC	N.D.	0.001 wt.%
5.2	ABS-FR, PVC	ABS/PVC	PVC	N.D.	0.001 wt.%
6.1	no info	PVC	PVC	N.D.	N.D.
6.2	no info	PVC	PVC	N.D.	N.D.
7.1	no info	PVC	PVC	N.D.	0.001 wt.%
7.2	no info	PVC	PVC	N.D.	N.D.

*Sample numbering: 1st number indicates the number of plastic housing and 2nd number indicates the number of sample **no info: No mark found, ***N.D.: Not Detected

Appendix G: Results of identification of vacuum cleaner samples by FTIR (OPUS/SEARCH and IDENT) by Fanari (2016) and results of reference XRF measurements.

	FTIR (OPUS/SEARCH)		FTIR (IDENT)		
Sample	**1st measurement**	**2nd measurement**	**1st measurement**	**2nd measurement**	**XRF (Bromine)**
1.1_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.**
1.1_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	0.001 wt.%
1.2_1	PP	PP	N.I.*	N.I.	N.D.
1.2_2	PP	PP	N.I.	N.I.	N.D.
1.3_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.3_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.4_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.4_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.5_1	PP	PP	N.I.	N.I.	N.D.
1.5_2	PP	PP	N.I.	N.I.	N.D.
1.6_1	ABS	ABS	ABS	ABS, 5 wt.% HBCD	N.D.
1.6_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.7_1	PP	PP	N.I.	N.I.	N.D.
1.7_2	PP	PP	N.I.	N.I.	N.D.
1.8_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.8_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.9_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.9_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.10_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.10_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.11_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.11_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.12_1	PP	PP	N.I.	N.I.	N.D.
1.12_2	PP	PP	N.I.	N.I.	N.D.
1.13_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS	0.003 wt.%
1.13_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS	0.004 wt.%
1.14_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.14_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.15_1	PP	PP	N.I.	N.I.	N.D.
1.15_2	PP	PP	N.I.	N.I.	N.D.
1.16_1	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.
1.16_2	ABS	ABS	ABS, 5 wt.% HBCD	ABS, 5 wt.% HBCD	N.D.

*N.I.: Not Identified, **N.D.: Not Detected

Appendix H: Results of identification of inkjet printer samples by FTIR (OPUS/SEARCH and IDENT) by Fanari (2016) and results of reference XRF measurements.

	FTIR (OPUS/SEARCH)		FTIR (IDENT)		
Sample	**1st measurement**	**2nd measurement**	**1st measurement**	**2nd measurement**	**XRF (Bromine)**
2.1_1	HIPS	HIPS	PS, DBDPE	PS	N.D*
2.2_1	HIPS	HIPS	PS	PS, DBDPE	N.D
2.3_1	PS	PS	PS, HBCD	PS	N.D
2.4_1	PS	PS, FR 100	PS, HBCD	PS, DBDPE	N.D
2.5_1	PS	PS, FR 100	PS	PS	N.D
2.6_1	PS	PS	PS	PS	N.D
2.7_1	PS	PS, FR 100	PS	PS	N.D
2.8_1	PS	PS	PS	PS	N.D
2.9_1	PC/ABS, FR 90	PC/ABS, FR 90	PS	PS	0.044 wt.%
2.9_2	PC/ABS, FR 90	PC/ABS, FR 90	PS	PS	0.048 wt.%

*N.D.: Not Detected