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# Further development of measuring brominated flame retardants in WEEE plastics

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# Kurzfassung

Elektroaltgeräte sind häufig mit bromierten Flammschutzmitteln (BFR) versehen, um bei Hitzeentwicklung dem Brand entgegenwirken zu können. Die europäische Gesetzeslage sieht bei EAGs Grenzwerte für den Gehalt an bromierten Flammschutzmitteln vor (1000 ppm für PBDE und 1000 ppm für PBB). Entscheidend für das Abfallmanagement von EAGs ist daher eine praktikable und zuverlässige Erkennung, ob ein Gerät, bzw. eine Gerätegruppe BFR enthält, oder nicht. Ein Ziel dieser Masterarbeit ist es, die Röntgenfluoreszenz-Analyse als Erkennungsmethode zu evaluieren und dabei 4 potenzielle Fehlerquellen zu untersuchen und das Ausmaß ihrer Einflüsse zu bestimmen: Die Oberflächenstruktur und Dicke der Probe, die Verteilung des Broms in der Probe, sowie die Software-Einstellung des XRF-Geräts. Die Ergebnisse zeigen, dass lediglich die Verteilung des Broms als Einflussfaktor auf das Ergebnis ausgeschlossen werden kann. In einem zweiten Teil werden 4 Produktgruppen auf ihren Gehalt an BFR untersucht: Mobiltelefone, Flachbildschirme, Elektrogroßgeräte und Küchengeräte. Während bei Mobiltelefonen, Flachbildschirmen und Küchengeräten Brom nachgewiesen werden konnte, waren die untersuchten Elektrogroßgeräte frei von Brom.

# Abstract

Waste electric and electronic equipment is frequently equipped with brominated flame retardants to counteract burning in case of high temperatures. To meet European waste management policies, WEEE plastics must not contain BFRs above a threshold limit of 1000 ppm for PBDE and 1000 ppm for PBB.

A key in managing e-waste is a reliable and practicable method to analyze whether it exceeds the threshold limit or not. One aim of this master's thesis is to evaluate XRF spectroscopy whether it is a useful method to measure BFRs in WEEE housings. 4 potential sources of error are analysed: The surface condition and the thickness of the sample, the homogeneity of the bromine within the sample and the software setting of the XRF device. The results show that only the distribution of bromine within the sample does not influence the measuring result, i.e. the bromine is added homogeneously. In a second part of this master's thesis 4 product categories are analysed in terms of their content of bromine: mobile phones, flat screens, large equipment and kitchen equipment. Some mobile phones, flat screens and kitchen equipment did contain bromine, while all large equipment samples were free of bromine.

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# List of abbreviations

| | |
|---|---|
| ANOVA | Analysis of variance |
| ABF | Institute of waste management, BOKU Vienna |
| ABS | Acrylonitrile butadiene styrene |
| ASA | Acrylonitrile styrene acrylate |
| ATH | Aluminium trihydrate |
| BFR | Brominated flame retardants |
| cps | Counts per second |
| CRM | Certified reference material |
| EEE | Electronic and electric equipment |
| FR | Flame retardant |
| FS | Flat screen |
| FS BS | Flat screen back side |
| FS FS | Flat screen front side |
| FTIR | Fourier transform infrared spectroscopy |
| HBCD | Hexabromocyclododecane |
| HFR | Halogenated flame retardant |
| KE | Kitchen equipment |
| LE | Large equipment |
| LOI | Limiting oxygen index |
| MP (O/N) | Mobile phone (old/new) |
| OPFR | Organophosphorus flame retardant |
| PBB | Polybrominated biphenyls |
| PBDE | Polybrominated diphenyl ethers |
| PC | Polycarbonate |
| PCB | Printed circuit board |
| PE (LDPE) | Polyethylene (low density polyethylene) |
| PET | Polyethylene terephthalate |
| pH | Peak height |
| PMMA | Poly(methyl methacrylate) |
| POP | Persistent organic pollutant |
| PP | Polypropylene |
| PPO | Poly(p-phenylene oxide) |
| PS (HIPS) | Polystyrene |
| PSU | Power supply unit |
| PUR | Polyurethane |
| PVC | Polyvinyl chloride |
| REACH | Registration, evaluation, authorization of chemical substances |
| RoHS | Restriction on Hazardous Substances Directive |
| SAN | Styrene acrylonitrile resin |

| | |
|---|---|
| SCoP | Stockholm Convention on POPs |
| TBBPA | Tetrabrom bisphenol A |
| WEEE | Waste electronic and electric equipment |
| wt-% | Weight in % |
| XRF | X-ray fluroescence (spectroscopy) |

# 1 Introduction

Electric and electronic equipment (EEE) becomes more and more pervasive in modern society. The number of sold electrical devices is rising from year to year. According to the Federal Waste Management Plan 211.000 t of EEE were put on the Austrian market in 2017 (that equals around 25 kg per inhabitant) (BMLFUW, 2019).

With the increase in demanding EEE the mass of electric and electronic waste rises as well. Due to the fast-technological development in this sector and high demands on new design, consumers often buy new products and get rid of their old items. An estimated amount of around 116.000 t of waste EEE was collected in Austria in 2017 (in 2008: 65.460 t) (BMLFUW, 2019).

Waste electric and electronic equipment (WEEE) is a waste fraction with complex properties in matters of their waste management. In the first place they are relevant because they contain a number of precious materials which are important for material recovery. For instance, indium is used in LCD panels, copper as wire and cobalt in Li-ion batteries. Mining these materials is difficult and expensive and can be, at least partly, replaced by recycling them from WEEE (Zhang et al., 2017).

On the other hand, many toxic substances such as heavy metals and flame retardants hinder or influence the recycling of WEEE (Buekens and Yang, 2014). Toxic heavy metals are used in EEE for many different purposes, e.g. as solder, in batteries or as pigments and therefore may appear in many parts of the devices. Flame retardants are added to reduce the flammability and occur exclusively in plastic parts of EEE. Beside their life-saving ability of reducing the combustibility of EEE, they are harmful to the environment and to human health when handled inappropriately (Stevens and Goosey, 2009).

Many different polymers are used in EEE. In about 30-35 % of all cases WEEE plastics are ABS, 20-25 % are HIPS and 20-30 % are PP (Haarman and Gasser, 2016).

The housings are often made of ABS, PC, PP; PCBs are mainly made of epoxy resins and consumer electronics are frequently made of HIPS. Table 1 shows EEE product categories and the dominating plastic types used for them. It is noticeable that all mentioned product categories may contain ABS. Almost all of the polymers used in EEE may contain brominated flame retardants (Buekens and Yang, 2014).

*Table 1: Dominating polymers in WEEE product categories. The table shows the most common plastic types per each EEE category. Relevant for this thesis are consumer electronics, IT devices, large and small appliances (Buekens and Yang, 2014).*

| Product category | Dominating plastic category |
|---|---|
| Consumer electronics | HIPS, ABS |
| Information technology devices | ABS, HIPS, ABS/PC, PPO/PS |
| Large electrical appliances | PP, PUR, ABS, PS, HIPS |
| Small electrical appliances | PP, HIPS, ABS |
| Cooling appliances | ABS, HIPS, PUR, PP, PVC |

Due to their health and environmental impacts, plastic parts should be treated carefully. Additionally, they might be ecologically problematic when used for energy recycling because toxic substances like dioxins and furans can be the result of the thermal process (Pivnenko et al., 2017).

To date, the recycling process of WEEE in state-of-the-art recycling plants, e.g. in developed countries, can be divided in 3 parts: (I) dismantling, (II) separating recyclables from hazardous materials/substances and (III) final treatment. When a device is classified as not reusable it enters the dismantling process where all parts, i.e. materials are getting disaggregated. In the optimal case all recyclables are then collected and prepared for a material recycling, e.g. by cleaning, granulating and melting. All non-recyclables are treated in an alternative way, e.g. by incineration for energy recycling. Plastic parts from WEEE either go into material recycling or incineration, in some cases they go directly into disposal, depending on its contamination with hazardous substances like flame retardants (Salhofer et al., 2016).

The fact that WEEE is often equipped with toxic substances is also important in developing countries, where WEEE is often treated by informal waste recyclers. The main objective of the informal recycling is to extract, homogenise, and subsequently sell valuable materials irrespective of the health implications for involved employees or environmental consequences. The treatment (e.g. burning for melting polymeric isolations to extract copper wire) usually takes place without the usage of masks, filters or hand gloves (Gupta, 2014). So, the brominated flame retardants might contaminate the environment and endanger the waste managers (Sthiannopkao and Wong, 2012).

From inappropriate incineration, that is, without sufficient filters brominated flame retardants may enter the environment. In this context, sufficient filters are defined as materials which absorb or separate toxic and further unintentional substances from smoke and dust in a manner which fulfils legislation. There is also the possibility of contamination via dust or when disposed inappropriately. They can enter the food chain by grazing cattle on contaminated soil or by fish in contaminated water. In human bodies they are suspected of being cancerogenic and endocrine disrupting (Kim et al., 2014).

However, toxic substances in WEEE are relevant for state-of-the-art waste management in developed countries. On the one hand, they may be effective on workers handling WEEE. Additionally, while the amount of WEEE is continuously rising, the European Union is raising the share of WEEE that has to be recycled (since August 2018 up to 80 % of collected WEEE have to be recycled or reused, depending on the product category). Additionally, a further lowering of the recommended threshold limits for brominated flame retardants in EEE plastics is under discussion due to their effects on the environment and human health. To comply with these requirements the recycling of plastic parts has to be optimized, this is relevant as the share of plastics in EEE amounts to ca. 20 wt% (Buekens and Yang, 2014).

To achieve the European goals, that is, to comply with the recycling quotas and displacing the toxic substances in recycled products, a fast method has to be evolved to identify flame retardants in plastic parts. Parts which are free of brominated flame retardants (BFR) can be recycled, those which are equipped with BFRs do not suit for material recycling and have to be treated differently (Buekens and Yang, 2014; Tange and Drohmann, 2005).

A fast and cheap method to identify brominated flame retardants can improve and quicken the process to categorize the plastic parts. Common analysing methods like gas chromatography and mass spectrometry are reliable instruments but do not satisfy the requirements of a quick and easy way to detect BFRs. A promising method seems to be the x-ray fluorescence analysis (Cocco, 2018).

Two foregone master's theses (Cocco, 2018, Fink, 2019) already analysed x-ray fluorescence as a method to identify flame retardants in plastic parts of WEEE. This paper aims to deepen the research.

This thesis is organised in two main parts. The first part, chapter 2, is a theoretical part whereas the second part, chapter 3, primarily deals with the experiments made. Chapter 2 examines why and how flame retardants and especially brominated flame retardants are used in EEE. It attends to its effects on environment and human health by focusing on the situation in developed countries, respectively at state-of-the-art waste management. Later on, the according European legislative situation is investigated.

Chapter 3 will cover the scope of the experimental part of this thesis. On the one hand, potential sources of error which may appear during the measurement will be analysed, containing the surface condition and thickness of the analysed sample, the distribution of the BFR within the sample and the software setting of the XRF device.

On the other hand, some WEEE categories will be analysed whether they contain BFRs and if they do so in what intensity. After explaining the used methods, the results of the measurement will be presented followed by a short summary and a discussion.

**The following research questions shall be answered with this thesis:**

(1) How is the measurement influenced by potential sources of error:

- surface condition
- thickness of the sample
- distribution of BFR in the sample
- calibration of the XRF-tool and used software

(2) What intensity of bromine can be detected in certain WEEE categories:

- kitchen equipment
- flat screens
- mobile phones
- large household equipment

The product category, however, was expected to be an important factor on the amount of measured Br. Devices, respectively certain parts of devices which reach higher temperatures will more likely contain Br (e.g. flat screens are more likely to contain Br than the display panel of a dishwasher).

# 2 Flame Retardants in WEEE

To reduce the danger of fire in EEE, for example due to a short circuit fault, its plastic parts are equipped with flame retardants. A flame retardant has to fulfil some specifications when used in EEE plastics. Firstly, it has to be economically efficient and easy to applicate without influencing the characteristics of the polymer too much. It should ensure the fire protection without producing toxic substances or increasing smoke when a fire starts to burn. Not having negative effects on health and environment and being recyclable are also important specifications but not all FRs come up with these features (SFT, 2009).

Whether an electronic device contains flame retardants, and how much, or not, strongly depends on the used plastic category. Some plastic categories are not very flammable itself, e.g. polytetrafluorethylene (Teflon) or polyvinylchloride (PVC). Other categories, which are often used in EEE, are more flammable, e.g. polyethylene (PE), polypropylene (PP) or acrylonitrile-butadien-styrene (ABS). A useful index to compare polymers relating to their flammability is the limiting oxygen index (LOI). The LOI describes the relative amount of oxygen that is required for a sample to burn. Polymers with a higher LOI are more fire-resistant. While Teflon has a LOI of 94% PP, PE and ABS, which are often used in EEE housings, all have an LOI between 18-19%. Thus, Teflon does not need as much flame retardant application as PP (Laoutid et al., 2009).

Additionally, the decision on adding a flame retardant or not is contingent upon the purpose of the device, respectively upon the product category. Especially products which reach higher temperatures are equipped with flame retardants, e.g. PSUs or PC housings. In 2002 an estimated amount of 25% of all EEE materials was equipped with flame retardants (Wäger et al., 2012).

Flame retardants can be either attached chemically (reactive) or physically (additive). Reactive FRs are added during the polymerisation and hence are integrated in the molecule structure of the plastic. The fire-proof polymer has a different molecule structure compared to the original polymer. Additive FRs a not integrated in the polymer structure, that is, they can easily leave the structure and contaminate the environment. Otherwise, they can be added more easily than the reactive FRs (Posner, 2005).

## 2.1 Flame retardant categories with a special focus on halogenated flame retardants

Different ways exist on how to classify flame retardants. In this paper a categorization in 4 different groups of flame retardants was chosen which are described shortly below. The choice of the flame retardant is mainly left to the producer and is influenced by economical, and practical factors, e.g. compatibility with the used polymer, (Kolias, 2016):

- inorganic flame retardants
- organo-phosphorus flame retardants
- nitrogen containing flame retardants
- halogenated flame retardants

Considering all fields of application (not only EEE) inorganic FRs are chosen in 51 % of all productions in the European Union. Organo-phosphorus FRs make about 18 %, followed by halogenated FRs with 17 %. All other applications, including nitrogen containing FRs as well as coatings, antimony oxide, etc. build the rest (Futterer et al., 2017).[1]

### 2.1.1 Inorganic flame retardants

Commonly used inorganic flame retardants are Al(OH)3 (aluminium hydroxide), also known as ATH and Mg(OH)2 (magnesium hydroxide). At high temperatures (min. of 204°C) they react to water and aluminium oxide (respectively magnesium oxide) in an endotherm reaction and hence counteract the combustion – H20 and Al2O3 (MgO) build a barrier and protect the plastic part (Giessmann, 2010). Beside the fact that it counteracts the fire it also reduces the formation of smoke. The chemical reactions are listed below:

$$Al_2(OH)_3 \rightarrow H_2O + Al_2O_3$$

$$Mg(OH)_2 \rightarrow H_2O + MgO$$

Inorganic flame retardants only perform well in high concentrations compared to the other FR categories, so to date they are not used very often in EEE plastic parts like housings. Correct appliance (particle size, proper dispersion in the matrix material) and coated fillers may reduce the amount which has to be used. This may increase the usage in EEE in the future (Bonnet, 2009; SFT, 2009).

Rather, inorganic flame retardants such as ATH are used in construction products like thermal insulating foams and roofing membranes as well as cable material formulations (Vaari and Paajanen, 2018).

### 2.1.2 Organo-phosphorus and nitrogen containing flame retardants

Different types of OPFRs exist, hence it is difficult to summarize their functionality. The main groups, however, are phosphate ethers, phosphonates and phosphinates. Generally, at high temperatures the OPFRs react to phosphorus acid and dehydrate the plastic parts (Laoutid et al., 2009). Commonly they are added physically and not chemically. Some OPFRs are toxic due to its cancerogenic, allergic or neurotoxic effects. They are also suspected of killing erythrocytes but to date there is not much data about their toxicity available. However, in comparison to brominated flame retardants OPFRs do not build toxic gases at high temperatures (in case of fire) (van der Veen and de Boer, 2012; Wei et al., 2015).

Typical OPFRs are triethyl phosphates, acryl phosphates (in PVC) and reactive phosphorus FRs (in PUR and PET). Over the last years, OPFRs have emerged in WEEE as an alternative to BFRs. Studies show an increase of OPFR emissions in developing countries as a consequence of worldwide BFR scepticism and bans (Matsukami et al., 2015).

Nitrogen containing flame retardants (like melamine) are the eco-friendliest group of flame retardants. At high temperatures they produce a voluminous, isolating coating which

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[1] There is no such data available only for WEEE.

protects the polymer from fire. Yet they are not much in use but there is some research going on which may lead to an increase in usage in future EEE (Kuhn et al., 2004; Lu and Hamerton, 2002). Especially flame retardants with a combination of nitrogen and phosphorus are object of current research (Zhang et al., 2015)

### 2.1.3 Halogenated flame retardants

Halogenated flame retardants are in use in EEE because of their efficiency and suitability in plastics and are typically based on bromine or chlorine (Kuhn et al., 2004). When a plastic part starts to burn a chemical chain-reaction occurs. The radical and thus highly reactive hydrogen atoms which occur during combustion decompose the polymer and produce free carbon which reacts, i.e. it burns with the atmospheric oxygen (Freegard et al., 2006). The chain-reaction can be expressed as follows:

$$H\cdot\ + O_2 \rightarrow OH\cdot\ + O\cdot\cdot$$

$$OH\cdot\ + O\cdot\cdot \rightarrow OH\cdot\ + H\cdot$$

The halogenated flame retardant is attached to impede this chain reaction as follows, whereas X is a halogen atom, mostly bromine, sometimes chlorine.[2] Under heat, bromine, respectively chlorine radials occur ($X\cdot$) which react with hydrocarbons (RH) to form HBr or HCl. These molecules react with hydrogen radicals and thus slow down the chain-reaction (Harrison, 2007):

$$RX \rightarrow R\cdot\ + X\cdot$$

$$X\cdot\ + RH \rightarrow R\cdot\ + HX$$

$$HX + H\cdot \rightarrow H_2 + X\cdot$$

$$HX + OH\cdot \rightarrow\ H_2O + X\cdot$$

With a share of about 40 % brominated flame retardants are the most used halogenated flame retardants in EEE. They have a good price-performance ratio and a high effectiveness. The most often used BFRs are, respectively were, polybrominated biphenyls (PBB), tetrabromine bisphenol-a (TBBPA), polybrominated diphenylethers (PBDE) and hexabromocyclododecane (HBCD) (Alaee et al., 2003; Novak, 2001). Figure 1 shows the occurrence of the different BFR types in e-waste in 2014. It can be seen that TBBPA is the most commonly used BFR, followed by PBDEs. PBBs are comparatively seldom in WEEE. A main cause for this fact is the legal situation which limits the use of certain substances, see chapter 2.3.

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[2] Chlorinated flame retardants are no object of this paper; thus, they are not further examined.

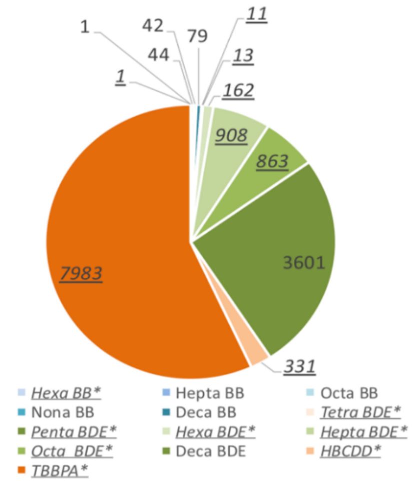

*Figure 1: Occurrence of different BFRs in WEEE in 2014. Almost 57 % of all used BFRs have been TBBPA which can be explained by the regulations on PBDE, HBCD and PBB. From all analysed BFRs (Hennebert and Filella, 2018)*

Brominated flame retardants can be divided in three categories, depending on their chemical structure: (I) aromatic, (II) cyclo-aliphatic and (III) aliphatic (Watson et al., 2010). Another way of classifying BFRs focuses on the fact that these substances, like all other flame retardants, can appear as an additive or a reactive mixture. Additive applications are cheaper but may have a softening impact on polymers, hence they are not always the preferred solution. Reactive applications, also called “backbone applications”, are more expensive, but they do not have a softening impact. Typical additive BFRs are PBDEs. As a reactive BFR TBBPA is most commonly used (Morf et al., 2007).

Ca. 56% of all BFR products are used in EEE, whereas 59% of them are attached in housing parts, 30% are used in PCBs, 9% in connectors and relays and the residual 2% are used in wires as can be seen in figure 2 (Herat, 2008).

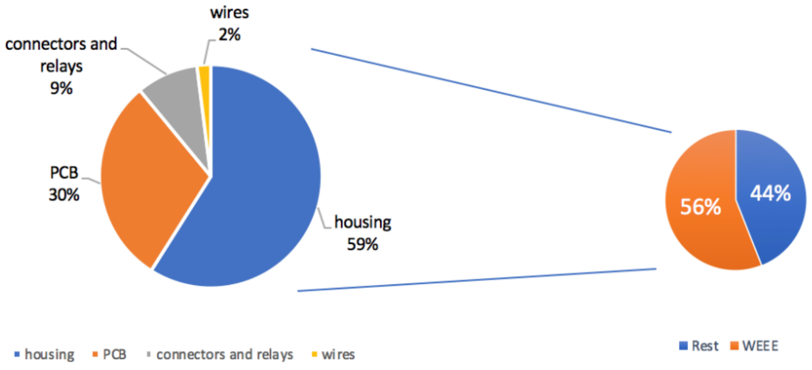

*Figure 2: Fields of application of BFR. 56 % of all BFRs have been used in EEE. The most common field of applications within EEE are housing parts with 59 %, followed by PCBs (30 %) and connectors and relays (in sum 9 %).*

The plastic category has an impact on the choice of the added brominated flame retardant. E.g. PBDEs (deca or octa) are typically used in PP, PE, HIPS and PA; TBBPA is typically used in ABS (Wäger et al., 2010).

But not only the type of the BFR depends on the plastic category but also the quantity of the BFR is contingent on it. There is no exact data available on how much BFRs are typically used in polymers. An application with a range of 1-30 wt-% is possible; typical amounts of PBDEs in ABS are 12-15 wt-%, to have a desired effect. There is an upper limit due to the instability of the polymer that goes along with the amount of added BFR. Adding too little amounts of BFR (< 1 wt-%) might be inefficient and thus does not fulfil fire resistance (Drage et al., 2018; Germer, 2008)

To enhance the effectiveness of BFRs (and flame retardants in general) chemical synergists are often added to the polymer. A commonly used synergist is antimony trioxide (Sb2O3). It facilitates the dissociation of halogens at high temperatures and therefore supports the fixation of radicals while it reacts with radicals itself. It appears in concentrations of 3-5 % in polymers (Freegard et al., 2006; Kuhn et al., 2004; Laoutid et al., 2009).

## 2.2 Brominated flame retardants as a risk for environment and human health

Bromine itself is a chemical element in the group of the halogens. In nature it appears only in bonds (usually as bromide). Elementary bromine is toxic and vitriolic. It may leave the brominated flame retardant and contaminate ecosystems (Sicius, 2016).

But brominated flame retardants are not only toxic when the extracted bromine enters the environment. BFRs can enter the environment in different ways: As an emission of EEEs containing BFRs during manufacturing, use, combustion or disposal. Due to its hydrophobic properties it can easily accumulate in sediments. In dismantling areas in China concentrations of PBDEs have been determined in water, atmosphere and biota (Yu et al., 2016).

As already mentioned above, additive BFRs can more easily leave the plastics. This fact is a typical path for so-called indoor exposure, which can be measured especially in recycling sites where WEEE containing BFRs is handled. Nevertheless, backbone BFRs may also lead to indoor exposure (Altarawneh et al., 2019).

Especially when handling WEEE plastics without certain protection brominated flame retardants may enter the environment. This is an important factor for informal waste management but also at professional waste management sites where concentrations of these substance could be determined in the environment (Sun et al., 2016).

At high temperatures BFRs have the ability to hinder EEE from ignition, respectively they may slow fire. On the other hand, BFRs may build dioxins and furans, normally at temperatures starting from 280°C. Dioxins and furans can occur at all stages of the life cycle of BFRs whenever high temperatures are reached, including the production, the usage, but especially at combustion. These substances are toxic to skin, immune system, reproduction and endocrine functions and may be cancerogenic. Though dioxins and furans may get destructed at higher temperatures (>700°C) in incineration sites, they can be built in flue gas (Zhang et al., 2016).

Subsequently, BFRs and its metabolisms can end up in human bodies. Some of them have a high bioaccumulation potential and can enter the food chain via grazing cattle on contaminated soil due to the inappropriate disposal of WEEE or via fish living in contaminated aquatic systems. They can also be absorbed via inhalation and through the human skin. The presence of PBDEs in food, especially in fish and processed food has been detected. In shellfish concentrations up to 2ng/g have been determined. In fish feed 1.2-4.6ng/g were measured (Fernandes et al., 2016).

Some microorganisms tend to metabolise the BFRs to some further toxic substances, e.g. TBBPA to BPA (bisphenol A). Table 2 summarizes the main characteristics of BFRs regarding their toxicity. That table does not span all available BFRs but shows properties of the most commonly used (Hartmann et al., 2016).

To date, not all BFRs are completely evaluated respecting their toxicity. At some points their impact on humans and the environment is not clear. But a high variability in toxicity of brominated flame retardants could already be determined (Usenko et al., 2016).

Not only the quality of impacts is incompletely investigated but also the quantity of exposure that has a toxic effect is not always evaluated. Foregone research tends that there is no linear relationship between the absorbed dose and health effects. In fact, the amount of health effects seems to be difficult to forecast (Kim et al., 2014).

The frequently used synergist antimony oxide is not suspected to be harmful to the environment but there are multiple studies which show a cancerogenic effect of antimony oxide on humans (Freegard et al., 2006).

*Table 2: Impacts and metabolism of commonly used BFRs. The characteristics are categorized in the ecological behaviour, the metabolism and the effects on human bodies (Freegard et al., 2006; Hartmann et al., 2016; Xie et al., 2018).*

| | HBCD | TBBPA | PDBE | PBB | Citation |
|---|---|---|---|---|---|
| **Ecological behaviour** | Persistent<br>High bioaccumulation<br>Transferable over high distances<br>Toxic to aquatic fauna | Persistent<br>Low bioaccumulation<br>Transferable over high distances<br>Toxic to aquatic fauna | Persistent<br>Toxic to aquatic fauna | persistent<br>Toxic to aquatic fauna | (Hartmann et al., 2016)<br>(Xie et al., 2018) |
| **metabolism** | n/a | BPA<br>Dioxins<br>furans | Dioxins<br>Furans | n/a | (Hartmann et al., 2016)<br>(Freegard et al., 2006) |
| **Effects to human bodies** | Toxic for thyroid<br>May influence reproduction<br>May contaminate children via breast's milk | Toxic for thyroid | Toxic for thyroid<br>Influences the endocrine system<br>neurotoxic | Skin sensitising<br>Toxic for liver<br>Cancerogenic | (Hartmann et al., 2016) |

## 2.3 Legislation on bromine in WEEE plastics

Over the years, many legal regulations have been developed to accomplish a diminution to the extent of a complete elimination of hazardous substances in WEEE. Over the time, national regulations are more and more driven by EU legislation. Some brominated flame retardants are already banned, some are limited in their concentration. This chapter aims to display a summary of the legal situation in the European Union regarding brominated flame retardants (Freegard et al., 2006). On the other side, the WEEE Directive regulates recycling quotas which also influence the BFR situation in WEEE and is explained in chapter 2.3.3.

### 2.3.1 Stockholm Convention on POPs

To accomplish and ensure the harmlessness of EEE some multinational conventions were modelled. In 2004, the Stockholm Convention on POPs (SCoP) entered into force which prohibits the use and emergence of specific substances, i.e. persistent organic pollutants, including some BFRs as well as dioxins and furans. Annex A of the SCoP lists all substances which are prohibited. Annex B lists all substances which shall not pass a certain limit and Annex C lists all uPOPs (unintentional POPs) which may occur under certain circumstances, e.g. at high temperatures. Currently, PBDE[3] and HBCD are listed in Annex A of the POP Convention, that is, they shall neither be produced nor used (Wäger et al., 2010).

The SCoP determines that all members have to take legal and administrative measures to execute the set regulations. (UNEP, 2017). Thus, the European Union which has ratified the SCoP created the POP Regulation (directive) and set certain limits for the BFRs registered by the Stockholm Convention. All member states of the EU have to follow this regulation which was firstly ratified in 2004 (EC, 2019).

Table 3 displays all BFRs and associated substances which are registered in the SCoP. In the third column all set limits by the European Union are listed. Next to thresholds for single BDEs a limit for the sum of BDEs is also set. When handling WEEE products which contain more than 1000 mg/kg, i.e. 1000 ppm of PBDEs this e-waste shall not be recycled before all PBDEs are eliminated or excluded (EC, 2019).

While some BFRs are already registered in the POP Convention, others are on the list to be under investigation. All member nations of the SCoP may recommend the registration of further substances. The Conference of Parties meets regularly to set new limits and prohibitions. It is assumed that more BFRs will be regulated in the POP Convention. Additionally, the EU discusses new limits for registered BFRs. Until July 16th 2021, the limit for the sum of PBDEs will be 500 mg/kg (EC, 2019).

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[3] tetraBDE, pentaBDE, hexaBDE, heptaBDE, decaBDE

*Table 3: BFRs and associated substances regulated by the Stockholm Convention on POPs in 2017, respectively by the POP regulation directive of the European Union (EC, 2019; UNEP, 2017).*

| SCoP-regulated substance | Regulation notes SCoP | POP regulation |
|---|---|---|
| ANNEX A - Elimination | | |
| decaBDE | Use: In EEE plastic housings max. 10 wt-%<br>Production: only registered nations | • Production, Use and placing on the market of products only with max. 10mg/kg per BDE (unintentional trace contaminant) → WEEE are specially regulated<br>• Usage is permitted when used since 25th August 2010 or earlier<br>• **Special regulation on substances in WEEE in RoHS**<br>• **Max. 1000 mg/kg sum of all BDEs in waste (special treatment needed, POPs have to be eliminated)** |
| hexaBDE | Recycling in a sound manner and no exports of products containing<br>• hexaBDE<br>• heptaBDE<br>• pentaBDE<br>• tetraBDE | |
| heptaBDE | | |
| pentaBDE | | |
| tetraBDE | | |
| HBCD | Use: allowed only in expanded polystyrene (not in EEE) | • Production, Use and placing on the market of products only with max. 100mg/kg per BDE |
| ANNEX C – Unintentional Production | | |
| PCDD/PCDF[4] | Both substances shall not emerge | Max. 15 µg/kg |

However, the Stockholm Convention recommends to separate WEEE which is equipped with listed BFRs from WEEE without listed BFRs. Since some unlisted BFRs are chemically pretty similar to listed BFRs the separation proves itself as complicated. Therefore, the Guidance Document of the SCoP recommends to analyse the Br content. (Haarman and Gasser, 2016).

### 2.3.2 RoHS-Directive and REACH-Directive

To minimize the negative impacts of hazardous substances in EEE the European Union additionally forbade the usage of some substances beyond a certain threshold in 2004 in its Restriction on Hazardous Substances Directive (RoHS) which firstly came into force in 2006. Besides 4 heavy metals (Cr IV, Pb, Hg and Cd) and some plasticizers (DEHP, BBP, DBP and DIBP) there are also 2 flame retardants on the list: It is not allowed to produce or import EEE containing more than 1000ppm PBDE or PBB referring to the mass in

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[4] Polychlorinated dibenzo-p-dioxins and dibenzofurans

homogenous material. All product which contain more of these substances have to be sorted out and are not allowed to be recycled. The limit for PBDEs conform to that set with the POPs Regulation. Instead of regulating HCBD the RoHS Directive regulates polybrominated biphenyls (EC, 2011). Additionally, the EU developed the REACH-Regulation to regulate the use and registration of chemical substances. Especially companies, which produce, import or use hazardous substances, are addressed with the REACH-Directive. They are committed to registrate their produced or imported chemicals like flame retardants (EC, 2006).

### 2.3.3 WEEE-Directive

The WEEE-Directive which became effective in 2013 aims the regulation of negative impacts of WEEE on humans and the environment. It aims a more sustainable production and usage of EEE. A main assignment is the “producers’ responsibility” which brings producers to think of ecological claims when designing a product (EC, 2012).

The member states are obliged to collect WEEE separately. This is an important preliminary work for a purposeful waste management of this waste fraction. The European Union defined collection quotas for WEEE. It also provides a quota of collected WEEE which has to be recovered[5] and an extra quota of WEEE which has to be recycled[6] as shown in table 4. All quotas are calculated by dividing the treated, respectively recycled mass of a WEEE category by the collected mass of this WEEE category (EC, 2012).

*Table 4: Recycling quotas and recovery quotas as regulated since 15th August 2018 by the European Union (EC, 2012)*

| Product category | Recovery quota (%) | Recycling quota (%) |
|---|---|---|
| **(1) temperature exchange equipment** | 85 | 80 |
| **(2) screens, monitors having a surface >100 cm$^2$** | 80 | 70 |
| **(3) lamps** | - | 80 |
| **(4) Large equipment > 50 cm** | 85 | 80 |
| **(5) Small equipment < 50 cm** | 75 | 55 |
| **(6) IT & telecommunication equipment** | 75 | 55 |

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[5] The recovery of waste is defined as any operation with waste which leads to a useful purpose of this waste by replacing other materials which would fulfil this purpose instead (e.g. for generating energy, recycling of metals etc.) (EC, 2008).

[6] The recycling of waste is defined as any recovery operations at which the waste material is not used for energy recover (EC, 2008).

Since many EEE products have a high share of plastics, e.g. small EEE consists of ca. 49 wt-% plastics, these plastic parts have to be under consideration when aiming to fulfil the recycling quotas of the WEEE-Directive. It is not possible to satisfy the recycling quota which is 55 wt-% for IT & telecommunication equipment without recycling at least some plastic parts (Martinho et al., 2012).

In principle, plastic parts from WEEE can be recycled if they satisfy some certain criteria. Beside e.g. the colour and the shrinkage probability, some substances which are added in the polymeric structure might hinder the recycling opportunities. Respecting the above mentioned legal regulations, some brominated flame retardants must be considered before recycling a WEEE plastic (Freegard et al., 2006).

The European Union tends to lower the threshold for bromine in WEEE. But it might be problematic to set the threshold limit at e.g. 0 ppm because this would make a recycling of polymers unpractical. Thus, a lot of WEEE plastics could not be recycled, since some are contaminated with a certain amount of bromine. However, the cutting of the maximal allowed amount of halogenated flame retardants in EEE on the one hand and the raising shares of WEEE which have to be recycled on the other hand require a fast and cheap method to identify BFR in WEEE plastics (Aldrian et al., 2015).

### 2.3.4 Management and recycling opportunities for WEEE containing BFR

After identifying brominated flame retardants in WEEE, BFR plastics can be separated from non BFR-plastics. BFR plastics are those with a bromine content higher than the legal limit, i.e. they have to be managed differently from those which are free from BFR (Freegard et al., 2006).

As already mentioned above, brominated flame retardants have to be added in a certain amount to perform well. A foregone study shows that WEEE often contains 0.1-1% bromine/BFR which is an inefficient amount referring to the flame retarding properties. It is assumed that these concentrations appear due to already recycled BFR plastics in plastic blends. In this case, the housings contain bromine without using its positive flame-retarding characteristics but cannot be recycled according to BFR regulations (Sindiku et al., 2015).

To fulfil the recycling quotas even with too high contents of brominated flame retardants, some alternative solutions might be suitable. One possibility of extracting the BFRs from the WEEE plastics is solvent extraction by using isopropanol and toluene. This technique may come into operation when managing WEEE plastics in a pyrolysis recycling procedure (Nnorom and Osibanjo, 2008).

Separating BRF-plastics from non BFR-plastics is a critical key for managing WEEE. There are some different techniques available. The following chapter copes deals with the analysis of BFRs in WEEE plastics.

# 3 Identifying bromine in WEEE by using XRF

The composition of samples can be analysed with different tools. Beside costly mass spectrometry (MS) and gas chromatography (GC) spectroscopic methods are in use. Spectroscopy describes an analysing method at which the sample is exposed to a certain radiation (UV, IR, etc) (Kolias, 2016).

The X-Ray Fluorescence Analysis (XRF) is a spectroscopic method. The XRF device emits x-ray radiation which stimulates the atoms in the sample. Some electrons from the inner shell get dislodged and replaced by electrons from higher energy levels. The nascent energy gets emitted by the atom and can be measured by the XRF device. The energy level of this radiation is unique for every element. Thus, bromine can be detected. The intensity of this measured energy can be used for calculating the concentration of Br. Figure 3 shall explain the procedure (Sharkey et al., 2018).

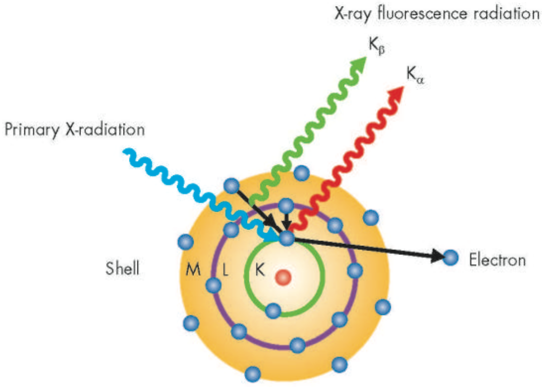

*Figure 3: Scheme of XRF emitting radiation and influencing a chemical element. The primary x-radiation, emitted by the XRF device, stimulates electrons of inner shells. These electrons might leave the atom and electrons from outer shells fill in the space. The nascent energy is emitted as fluorescence radiation and can be detected by the XRF device. Every atom has its unique fluorescence radiation. Thus, the element can be determined (Fischer, 2019).*

XRF is a spectroscopic method using x-ray radiation with several advantages. Firstly, a handheld-XRF is a mobile device and thus used on-site which is practical for recycling sites. A further advantage is its ability to analyse samples without destructing them. In contrast, GC and MS are both analysis techniques at which the samples get vaporized. Its detection limit lies between 10 and 100 ppm for elements which is accurate enough regarding the BFR legal framework (Haarman and Gasser, 2016).

Due to its practical characteristics, the XRF may be a useful method for future measurements to analyse whether a WEEE is equipped with BFRs or not. Additionally, it might be useful to identify the BFR concentration. But there might be some limiting factors which influence the analysis and therefore falsify measurement results. (Aldrian et al., 2015).

## 3.2 Procedure

The analysis was done in the following steps: Samples of 4 product categories have been purchased. The choice of the devices was done randomly. After collecting the devices, their main characteristics have been documented, e.g. colour, brand and model name. In a next step, the devices, i.e. the devices have been dismantled to extract subsamples from the housings. These subsamples were used for the actual analysis. Figure 4 shows the sampling procedure.

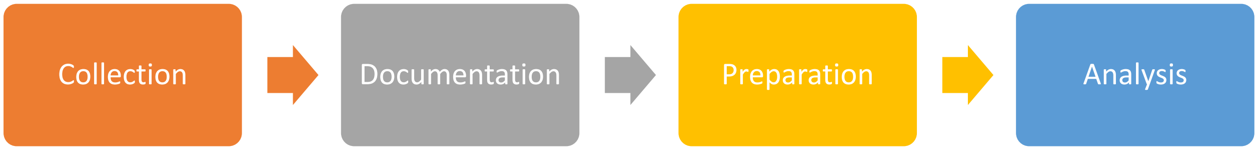

*Figure 4: Scheme of the sampling procedure. After collecting the devices from three different waste management facilities, they were documented. In a next step, subsamples have been extracted which were then used for the XRF measurement.*

The devices have been received from one of three reuse and recycling facilities, all located in Vienna:

- Demontage- und Recyclingzentrum (DRZ): kitchen equipment
- Reparatur- und Servicezentrum (RUSZ): large equipment, flat screens
- Austrian Red Cross: mobile phones

There is no information available where these products have been bought or how long they have been in use. Especially the information on the location of purchase might have been interesting, since some countries do not follow neither the Stockholm Convention nor the EU regulations on WEEE and BFR. Additionally, there was no prior check on whether the products still work or not. It can be assumed that all products were disposed in Austria as all sample donors (DRZ, RUSZ and Austrian Red Cross) are Austrian facilities which handle Austrian waste primarily.

The purchased samples have been documented in a first place. The documentation included the registration of the brand and the name of the model. In some cases, the name of the model could not be determined. All samples have been photographed for documentation purposes.

Subsequently, all samples have been tagged. An example shall clarify the tagging: A given sample represents an old mobile phone (MP_O). The first documented mobile phone got the number “1” and thus had the unique tag “MP_O_1”, the second old mobile phone got the tagging “MP_O_2” and so on.

After documenting the samples, they all got dismantled to extract the plastic housings. The dismantling process took place either at the ABF or directly at the recycling site (RUSZ). The preparation was done by using several tools, e.g. screwdrivers, grippers and scissors. By means of visual and haptic attributes the different parts could be separated following Dimitrakakis et al. (2009). Thus, for the further analysis relevant plastic housing parts could be separated. The housings of some samples could not be extracted or were not made out of plastic but metal and therefore were not relevant for the analysis. These samples have not been considered for the analyses. Object of investigation where the housings, thus, the residual parts of the samples were not used for further examinations.

Table 5 displays the number of all analysed samples. Column B shows the defined subcategories and column C shows the associated abbreviations which were used for the tagging. In total, 125 samples have been analysed. Connatural samples have been merged in subcategories. Thus, a further categorization has been generated as can be seen in table 5.

*Table 5: Analysed product categories in this thesis. The 4 evaluated product categories were structured in subcategories. In total, 125 samples have been analysed.*

| **Product category (total sampling nr)** | **Subcategory** | **Abbreviation** | **Number of samples** |
|---|---|---|---|
| Mobile phones (32) | Old mobile phones | MPO | 18 |
| | Smartphones | MPN | 14 |
| Large Equipment (10) | Washing machines | LE | 5 |
| | Dishwashers | | 5 |
| Flat screens (54) | Front side | FS_FS | 27 |
| | Back side | FS_BS | 27 |
| Kitchen equipment (29) | Stick blender | KE | 3 |
| | Toaster | | 8 |
| | Mixer | | 4 |
| | Kettle | | 6 |
| | Coffee machine | | 6 |
| | Juice Extractor | | 1 |
| | Cutter | | 1 |

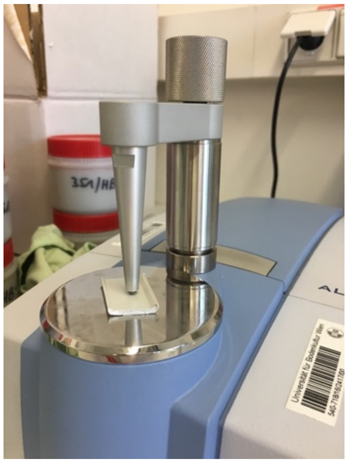

*Figure 5: Arrangement of the infrared analysis of a subsample for identifying the plastic type of the sample.*

After dismantling the samples and separating the plastic housing parts, subsamples of every sample have been extracted to identify the plastic type. Although, many samples, especially the newer products, fulfilled the obligation to label the plastic type, these were also analysed to eliminate the risk of a wrongly labelled product.

To identify the plastic type, all samples have been analysed with FTIR. The infrared measurements were executed with an FTIR spectrometer (Alpha II, Bruker Corporation, Billerica, USA) with an attenuated infrared reflexion technique using OPUS software for evaluation. All subsamples have been cleaned with a tissue and measured three times. The measured values have been normalized and averaged. The spectres have been interpreted by the FTIR software and by using Jung et al. (2018) as a comparison sheet for the spectrums. The plastic types of some subsamples where not possible to identify neither with the software nor by interpreting their spectra with Jung et al. (2018). These subsamples were marked “n/a” in the columns “Material” in the following result tables. Figure 5 shows a subsample of a flat screen being analysed with the FTIR device.

In a next step, the preparation of the samples, subsamples have been cut out of the samples for executing the measurement with the XRF. One subsample was taken from each sample for the analysis of its bromine concentration. The subsamples had to be small enough to fit in the XRF measurement chamber. To minimize the potential falsification of the results due to dirt, all samples have been cleaned with a cloth, some extremely dirty samples have been cleaned with water and a cloth. Figure 6 shows that one subsample has been cut out for the FTIR analysis to identify the plastic type and one subsample has been cut out for the XRF analysis. Since the FTIR analysis allowed smaller subsamples than the XRF analysis, two different subsamples have been used.

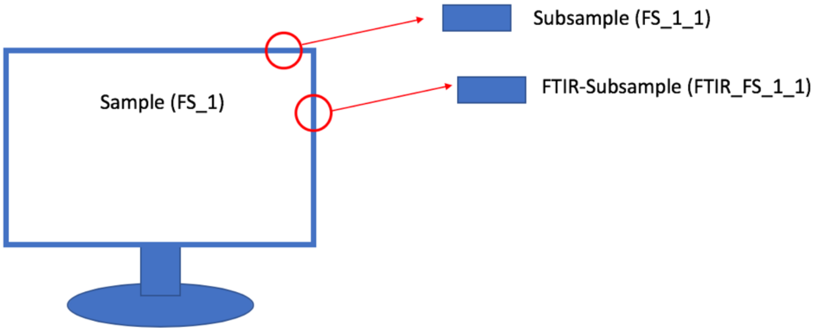

*Figure 6: Extraction of subsamples using the example of a flat screen. One subsample has been extracted from every device to analyse the content of Br by using XRF. Another subsample has been extracted to evaluate the plastic category by using FTIR.*

### 3.2.1 Sample preparation

For answering research question 1, some certain preparations had to be done which will be explained in the following sections.

#### *3.2.1.1 Surface condition*

The surface condition of the samples might have an impact on the result of the measurement. A large surface of a sample compared to its volume could hinder the fluorescence radiation from hitting the XRF detector. This might lead to a lower detected concentration than the actual concentration of Br within a sample. Thus, the surface condition of some samples has been changed to evaluate a potential impact (Haschke and Flock, 2017).

2 samples have been used to analyse the surface condition as a source of error: A flat screen sample which has already been tested positive on Br (see chapter 3.3), as well as certified reference material (ERM-EC590[7]). 3 different surface conditions have been considered in this analysis: (I) The untreated sample. In the case of the flat screen subsample, it was the bare subsample without any further preparations. The used CRM was a granulate of 2-3mm thick pieces. (II) A granulate with a higher surface than the untreated sample. (III) A pellet with a lower surface than the untreated sample.

The flat screen sample has been cut into pieces <0,5cm2 and then granulated with a centrifugal mill (Retsch, ZM 200) at 1600 rpm by using a distance sieve. To reduce the heat dissipation during the milling process some carbon dioxide snow has been added. Additionally, the samples were cooled to harden the plastic. Otherwise, high temperatures could have led to a melting of the sample. The ERM-EC590 had not to be cut in smaller pieces but was also milled in the same way. When using a normal sieve without a distance to the rotators, an intensive melting by the sample was observed which could have led to a dissolving of some BFRs and thus could have influenced the measuring results. The milled granulate has a larger surface than the untreated sample. The pellets have been produced by pressing some granulate to diminish the surface to a minimum. To press the

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[7] European Reference Materials, Belgium (ERM – EC590), see chapter 3.1.2.

pellet, some granulate of the CRM as well as from the sample has been pressed under a pressure of 10.000 t for at least 2 minutes following Haschke and Flock (2017).

Table 6 shows the line-up for this analysis. In the end of the preparation work, both samples were existent in all three conditions (the appendix of this thesis offers some pictures to illustrate the procedure).

*Table 6: Overview of objects for evaluating the structure and thickness as a potential source of error*

| **Sample** | **Subsample 1** | **Subsample 2** | **Subsample 3** |
|---|---|---|---|
| **ERM-EC590** | Untreated Subsample | Granulate | Pellet |
| **FS_FS10** | Untreated Subsample | Granulate | Pellet |

### *3.2.1.2 Thickness of the sample*

To evaluate the thickness as an impact on the result, pellets with different thicknesses have been pressed from ERM-EC590 in the same way as described in chapter 3.1.1.1. A certain mass of granulate ((I) 0,09 g, (II) 0,16 g, (III) 0,33 g, (IV) 0,5 g, (V) 0,7 g) has been used to press the pellets which led to subsamples with different thickness. Additionally, another CRM, BAM-H010[8], was also used to analyse the thickness as a source of error. Since this CRM was already existent in pellets, the pressing procedure could be skipped.

In a next step, some granulate from sample FS_FS10 which was already prepared for evaluating the surface condition, has been pressed to pellets of different thickness. These pellets were also used for evaluating the thickness as a source of error. It is important to mention, that the CRMs as well as the flat screen had a different matrix due to diverse plastic types and a different density due to their chemical structure. Even though, they were all pressed under the same circumstances, the pellets were not completely even regarding their density. The different matrix of the samples was also an influencing factor for the stability of the pellets. While the flat screen pellets were solid and stable, the ERM-EC590 pellets were unstable. Figure 7 shows the pressed pellets of the flat screen sample. The thickness increases from left to right; the left pellet is the thinnest one.

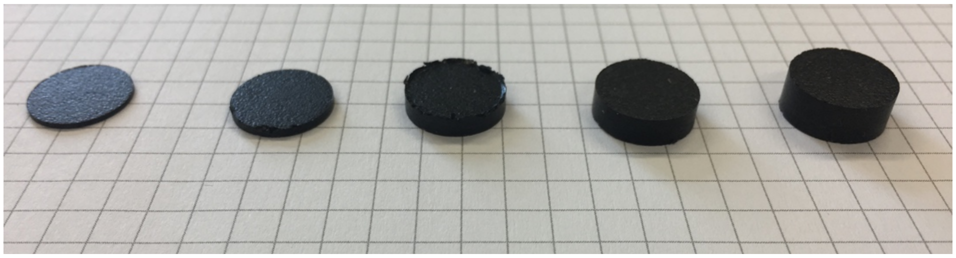

*Figure 7: 5 Pellets of different sizes of granulated sample FS_FS10. The thickness of the pellets increases from left to right.*

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[8] Bundesanstalt für Materialforschung und -prüfung, Germany (BAM H010), see chapter 3.1.2.

*Table 7: Overview of pressed pellets for analysing the sample thickness as a potential source of error*

| Sample | Subsample 1 (mm) | Subsample 2 (mm) | Subsample 3 (mm) | Subsample 4 (mm) | Subsample 5 (mm) |
|---|---|---|---|---|---|
| **FS_FS10** | 0,8 | 1,3 | 2,7 | 4 | 5,5 |
| **ERM-EC590** | 1 | 2 | 6 | 7,7 | 10 |
| **BAM-H010** | 1 | 2 | 6 | - | - |

For a better overview, table 7 summarizes the prepared pellets for analysing the sample thickness as a potential source of error.

#### *3.2.1.3 Homogeneity*

To analyse the distribution of bromine as a potential source of error, some samples which were checked positive on Br have been used to take additional subsamples from.

Thus, subsamples from different spots of the devices have been taken to analyse whether the BFR is added homogeneously. In principle, the samples which were used for answering this question were picked randomly. But there were some restricting factors. Some samples could not be used because there housing parts were too small to take 5 subsamples from. Especially the product category of mobile phones was confronted with this restriction. Some other samples were too tricky to take further subsamples from, e.g. the shape of the samples hindered the cutting.

Respecting these restricting factors, 5 samples have been chosen for this analysis. All of them were flat screen samples, because this product category had the most samples equipped with BFR. 4 of these samples were flat screen backsides, 1 was a flat screen frontside.

#### *3.2.1.4 Software and calibration*

The XRF device software offers different opportunities for the measurement, respectively for processing the measured data. The measurement program was also part of the analysis, whereas two programs have been tested: the soil mode and the plastics mode. The plastic mode could be used due to the fact that all analysed subsamples are made of plastics. Both modes have a different filter setting. Thus, the results of one sample measured in both modes show different intensities for bromine.

For this purpose, PSU[9] samples have been measured in the plastics mode and in the soil mode. PSUs have been chosen due to the fact that these products are often equipped with BFR. The results of the two measurements were then compared.

In the plastics mode the software offers a thickness correction mode. To analyse the accuracy of this mode, it was tested by measuring BAM-H010 with given thicknesses.

All analyses for this research question did not afford further sample preparations, because the settings were all chosen directly on the device.

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[9] PSUs: Power supply units from printers

### 3.2.2 Measuring method and interpretation of the data

After preparing the subsamples, they were ready for the analysis. All measurements have been executed with a Niton handheld device (XL3T950, Thermo Scientific Portable Analytical Instruments Inc., Tewksbury, USA) with a voltage of max 50kV. and a current of max 100 µA. The subsamples were put in the analysing chamber while the XRF device has been controlled via PC as seen in figure 8. The analysing chamber isolates the radiation and therefore the potential risk that goes along with x-rays and reduces the background which might decrease the quality of the measuring data.

To minimize the loss of radiation, every sample was put in the chamber as flat as possible to minimize the space between the bearing area and the sample following the results from Cocco (2018).

The measurement time, which was also already evaluated by Cocco (2018), was set to 50 seconds. Though, the peak of the intensity was evaluated to be reached at ca. 30 seconds, a longer measurement time has been chosen to avoid the risk of a loss of data quality.

Except some measurement regarding to research question 1 (see chapter 3.2.1.3) which was done in the plastics mode, all measurements were executed in the soil mode. The filter was always set on standard. All other settings have been set to default.

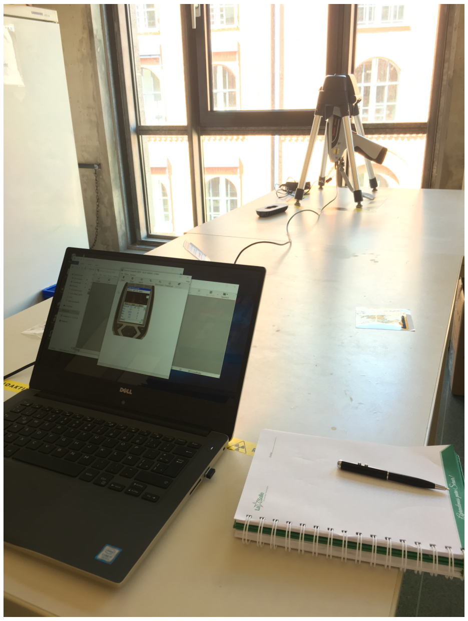

*Figure 8: Arrangement of the analysis. The XRF device was attached on the bottom of the analysing chamber. The sample was set directly on the detector of the XRF device. The measurement was controlled by a linked PC.*

All subsamples have been measured 3 times. The mean values of these 3 measurements have been used for the following statistical analysis.

To evaluate the measuring of the content of Br within a sample, it can be distinguished between a qualitative and a (semi-)quantitative analysis. The qualitative analysis is used to determine whether a sample contains Br or not. The existence of Br within a sample can be determined by 2 peaks in the spectrum: The first one, ka (kα) at 11.92 keV and the second one, kb (kβ), at 13.29 keV (Cocco, 2018).

The XRF analysis delivers the intensity of elements expressed in counts per second. To distinguish between the output of the XRF analysis and the actual Br concentration within a sample, the output is called "intensity" in this paper. The intensity describes the maximum peak height at 11.92 keV, which is the energy level of Br fluorescence radiation, expressed in counts per second. The actual Br concentration within a sample is named "concentration" in this paper.

Following Cocco (2018), a ka/kb ratio > 6 verifies a content of bromine within the sample. In the following tables which show the results of the measurements the results which fulfil this circumstance are coloured blue, all others are not coloured. I.e. all blue coloured samples contain Br and therefore are equipped with brominated flame retardants.

For the quantitative analysis ka can be used for calculating the BFR concentration. This value, the intensity of Br, could then be converted in the Br concentration expressed in ppm. To find the conversion factor, certified reference material (CRM) with a certain amount (concentration) of Br was used. One CRM (BAM-H010 – 1mm) was delivered by Bundesanstalt für Materialforschung und -prüfung, Germany. It is an ABS-pellet with a known concentration of Br of 240 ± 21 ppm. Additionally, a second CRM was used, delivered by European Reference Materials, Belgium (ERM – EC590) with a known concentration of 2130 ± 90 ppm. This CRM is made out of LDPE.

The bromine intensity of both CRMs can be measured with XRF. The measured intensity can be compared to the known concentration (ppm) to find the conversion factor. This conversion factor might be influenced by some sources of error.

Brominated flame retardants are not solely Br, but also other elements, the concentration of Br has to be converted in the concentration of Br. Aldrian et al. (2015) developed a model to convert the concentration of Br into the concentration of brominated flame retardants. They stated that 1000 ppm of brominated flame retardants contain ca. 820 ppm Br (Aldrian et al., 2015). Thus, the concentration of Br (ppm) has to be multiplied by the factor 0,82. Crucial for a qualitative analysis is the RoHS threshold limit which is set at 1000ppm for the summarized content of BFRs within a homogeneous plastic part. Correspondingly, a Br content of > 820 ppm means that a sample exceeds the threshold limits set by the European Union. Therefore, it cannot be reused or recycled without considering its content of brominated flame retardants.

## 3.3 Results

The following section shows the results from analysing the potential sources of error. After displaying the results from evaluating the surface condition and the sample thickness, the results regarding to the homogeneity of Br within a sample and the software mode are shown.

### 3.3.1 Surface condition

The preparation procedure described in chapter 3.2.1.1. led to subsamples (ERM-EC590 and FS_FS10), each with 3 different surface conditions: untreated, granulated and pellet. Table 8 shows the results of this analysis. Column B shows the measured peak heights of ka. It can be seen that the intensities of Br in sample FS_FS10 vary, although not to a large extent (92,0-98,4 cps). The ERM-EC590 samples show a much higher variety while the untreated sample shows the highest intensity of Br (605,8-798,6 cps) and the untreated CRM shows the highest intensity.

Figure 9 shows the results as a bar chart which visualises the differences of the impact of the surface condition on the measuring result. Having a look on the CRM samples, the measuring results differ in a larger extent than at the flat screen samples which contain less bromine. This higher influence may occur due to the general higher Br concentration of the CRM.

However, even at lower intensities the surface condition shows an impact on the measuring result, as can be seen for the flat screen sample. Thus, the impact of the surface condition on the Br intensity cannot be ignored in a quantitative analysis as it has an impact on the measuring result.

*Table 8: Results of measuring CRM and a flat screen sample with 3 different surface conditions.*

| **sample** | **Mean pH ka (cps)** |
|---|---:|
| **ERM-EC590 untreated** | 798,62 |
| **ERM-EC590 granulated** | 639,27 |
| **ERM-EC590 pellet** | 605,75 |
| **FS_FS10 untreated** | 94,01 |
| **FS_FS10 granulated** | 98,41 |
| **FS_FS10 pellet** | 92,88 |

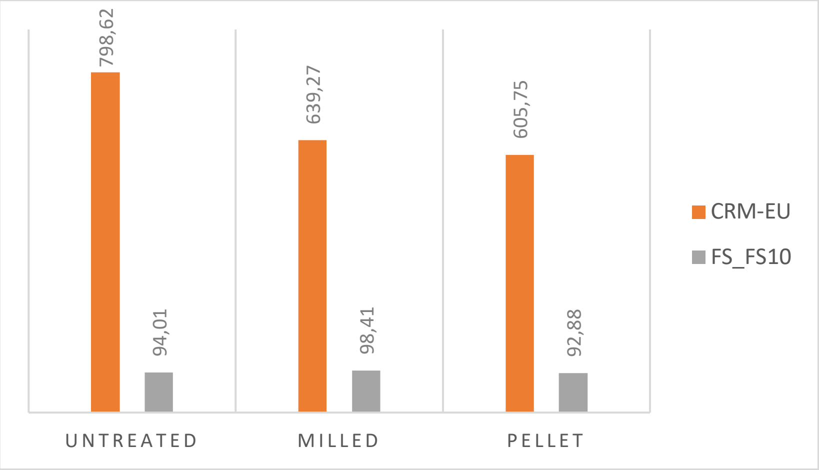

*Figure 9: Results of measuring CRM and a flat screen sample with 3 different surface conditions. The bars show a difference between the measured bromine intensity due to a change of the surface condition.*

### 3.3.2 Sample thickness

The sample thickness has been analysed as a potential source of error by 3 different samples: 2 CRM samples (ERM-EC590 and BAM-H010) and a flat screen sample (FS_FS10). Table 9 shows the thickness of all pressed pellets (mm) as well as the measured intensity (cps). The ERM-EC590 results are coloured light blue, the BAM-H010 results are coloured light green and the flat screen sample results are coloured yellow. It can be seen that the impact decreases with the abatement of the thickness. In other words, by increasing the sample thickness the measured intensity of the sample seems to reach a plateau. At some point (ca. at 7 mm), the impact of the sample thickness on the measuring result seems to be negligible.

As it is always the same granulate of each sample, the concentration, respectively the intensity of Br should be the same in all subsamples of one sample. While the thinnest pellet of ERM-EC590 (1 mm) shows an intensity of ca. 230 cps, the thickest pellet (10 mm) shows an intensity of ca. 699 cps. The BAM-H010 has an intensity of ca. 53 cps – ca. 136 cps, the flat screen samples have an intensity of ca. 35 cps – 105 cps.

Figure 10 shows the thickness correction factors of all measured values as spots. That is, the pellet of a sample with the highest measured intensity has the factor 1. When another pellet shows the half of this intensity, its thickness correction factor would be 0.5. The x-axis shows the subsample thickness.

The dashed lines show a logarithmic trend of the thickness correction factor of each sample. It can be seen that the slopes of the models are different. Thus, the correlation between the thickness correction factors and the thicknesses are not the same for all analysed samples. Creating a thickness correction model for all samples would be unprecise. So, no model has been created in this thesis.

*Table 9: Measuring results of all samples used to identify the thickness as a potential source of error.*

| **subsample** | **sample** | **thickness (mm)** | **intensity (cps)** |
|---|---|---|---|
| **1** | ERM-EC590 | 10 | 698,5825807 |
| **2** | ERM-EC590 | 7,7 | 664,284566 |
| **3** | ERM-EC590 | 6 | 586,717346 |
| **4** | ERM-EC590 | 2 | 369,320526 |
| **5** | ERM-EC590 | 1 | 229,9923043 |
| **6** | BAM-H010 | 6 | 135,66 |
| **7** | BAM-H010 | 2 | 104,76 |
| **8** | BAM-H010 | 1 | 53,49 |
| **13** | FS_FS10 | 5,5 | 105,151083 |
| **12** | FS_FS10 | 4 | 110,39798 |
| **11** | FS_FS10 | 2,7 | 93,654818 |
| **10** | FS_FS10 | 1,3 | 54,987863 |
| **9** | FS_FS10 | 0,8 | 35,482564 |

However, this finding leads to the perception that the intensity is not only dependent on the thickness of a sample. Another influencing characteristic may be the matrix of the sample. While the flat screen sample and the BAM-H010 pellets are both made of ABS, their thickness correction models are contiguous compared to the model of the HDPE made ERM-EC590 pellets. This perception goes in accordance with the described sources of error by Haschke and Flock (2017) who state that the thickness as well as the plastic matrix have a high impact on the measuring result.

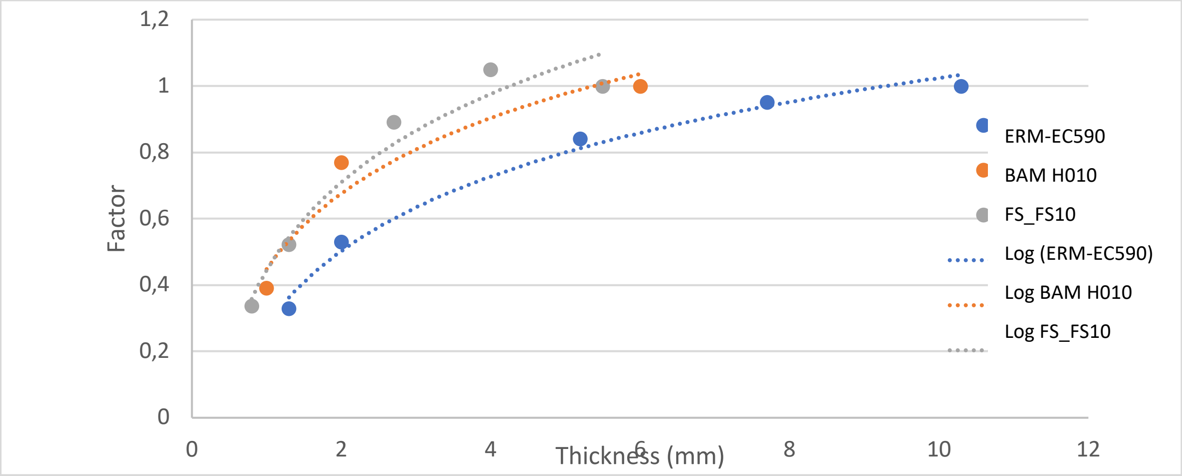

*Figure 10: Influence of sample thickness on the measured intensity of Br. The x-axis shows the thickness (mm), the y-axis shows the correction factor in relation to the intensity of the thickest subsample of each sample. logarithmic functions show a trend.*

### 3.3.3 Homogenity

Another analysed potential source of error is the distribution of the bromine within the sample. It might be possible to measure a certain amount of bromine on a spot of a sample which is not representative for the whole product because the BFR is added heterogeneously. So, some spots of the device feature a higher intensity of Br and thus have a higher concentration of Br than other spots. To evaluate this potential source of error, 5 devices which were already checked positive on Br were measured on 5 different spots. The analysed samples were 5 flat screens: 4 backsides, BS; 1 frontside, FS. Table 10 shows the results of these analyses. It presents the results per each sample. It can be seen that the standard deviation of the intensity of Br at different spots is low compared to its mean value (max. coefficient of variation = 7 % at sample BS_6).

*Table 10: Results of measuring BFR equipped samples on different spots. Each sample has been measured on 5 subsamples.*

| sample | mean | sd |
|---|---:|---:|
| **BS_2** | 536,15 | 21,26 |
| **BS_5** | 62,25 | 2,00 |
| **BS_6** | 113,29 | 8,22 |
| **FS_10** | 92,16 | 2,77 |
| **BS_20** | 130,37 | 4,13 |

To evaluate the impact of the distribution more in detail, an ANOVA has been executed. The underlying null hypothesis describes the fact that the choice of the measured spot has no significant impact on the measuring result. Table 11 shows the results of the ANOVA. The p value equals 2e-16, whereby this hypothesis could be accepted with a confidence interval of 95 %. Thus, the distribution of the bromine can be predicted as homogeneously added to the housing and has not to be considered when analysing Br concentration of plastic parts.

*Table 11: Results of the ANOVA for evaluating the impact of the distribution within a sample.*

| | Df | Sum Sq | Mean Sq | F value | Pr(>F) | |
|---|---:|---:|---:|---:|---|---|
| **sample** | 4 | 775519 | 193880 | 1769 | <2e-16 | *** |
| **Residuals** | 20 | 2192 | 110 | | | |

### 3.3.4 Software

To answer the question whether the software settings have an impact on the output, PSU samples have been measured, in the soil mode on the one hand, in the plastic mode on the other hand. Table 12 shows the results of all measured PSU samples. The results from measuring in the plastics mode are coloured blue, those which were measured in the soil mode are coloured green. Some samples which were checked positive on Br in the soil mode (ka/kb ratio > 6) could not be identified as Br equipped in the plastics mode in the same procedure, since no samples showed a ka/kb ratio > 6 in the plastics mode. Thus, the plastics mode is not a useful method for a qualitative analysis whether a sample contains Br or not by checking the ka/kb ratio.

*Table 12: Results of measuring the Br intensity of PSU samples in the plastics mode and in the soil mode.*

| **Button** | **Mean-PH-Ka** | **STD-PH-Ka** | **CV%-PH-Ka** | **Mean-Ka/Kb** | **mode** | **Mean-PH-Ka** | **STD-PH-Ka** | **CV%-PH-Ka** | **Mean-Ka/Kb** | **mode** |
|---|---|---|---|---|---|---|---|---|---|---|
| **PSU1** | 13,46 | 1,06 | 7,87 | 1,10 | plastics | 100,12 | 1,69 | 1,69 | 6,09 | soil |
| **PSU2** | 7,92 | 0,13 | 1,61 | 0,83 | plastics | 1,61 | 0,04 | 2,40 | 0,73 | soil |
| **PSU3** | 14,69 | 1,89 | 12,86 | 1,45 | plastics | 7,01 | 0,10 | 1,49 | 2,68 | soil |
| **PSU4** | 23,07 | 1,95 | 8,45 | 2,18 | plastics | 2,22 | 0,20 | 9,12 | 0,90 | soil |
| **PSU5** | 7,64 | 0,94 | 12,35 | 0,80 | plastics | 104,45 | 0,89 | 0,85 | 6,28 | soil |
| **PSU6** | 8,33 | 0,80 | 9,59 | 0,82 | plastics | 6,11 | 0,15 | 2,42 | 2,29 | soil |
| **PSU7** | 7,55 | 0,45 | 6,01 | 0,77 | plastics | 81,86 | 2,57 | 3,13 | 6,03 | soil |
| **PSU8** | 7,64 | 0,54 | 7,13 | 0,62 | plastics | 1,66 | 0,09 | 5,36 | 0,76 | soil |
| **PSU9** | 6,61 | 0,82 | 12,41 | 0,70 | plastics | 85,52 | 2,05 | 2,40 | 6,05 | soil |
| **PSU10** | 6,58 | 0,49 | 7,45 | 0,76 | plastics | 15,14 | 0,75 | 4,95 | 4,04 | soil |
| **PSU11** | 9,04 | 1,56 | 17,25 | 0,91 | plastics | 48,01 | 0,02 | 0,05 | 6,00 | soil |
| **PSU12** | 9,55 | 1,84 | 19,25 | 0,87 | plastics | 26,83 | 0,95 | 3,54 | 5,00 | soil |
| **PSU13** | 15,24 | 1,87 | 12,28 | 1,60 | plastics | 161,33 | 4,31 | 2,67 | 6,23 | soil |
| **PSU14** | 17,28 | 0,20 | 1,15 | 1,53 | plastics | 182,93 | 5,54 | 3,03 | 6,56 | soil |
| **PSU15** | 7,52 | 0,09 | 1,22 | 0,74 | plastics | 2,79 | 0,24 | 8,57 | 1,19 | soil |
| **PSU16** | 10,44 | 1,12 | 10,71 | 1,01 | plastics | 60,09 | 0,71 | 1,18 | 5,96 | soil |
| **PSU17** | 6,32 | 0,97 | 15,32 | 0,77 | plastics | 8,50 | 0,26 | 3,01 | 3,77 | soil |
| **PSU18** | 9,86 | 1,29 | 13,11 | 0,97 | plastics | 61,46 | 0,94 | 1,52 | 6,00 | soil |
| **PSU19** | 7,27 | 1,66 | 22,78 | 0,75 | plastics | 1,46 | 0,03 | 2,03 | 0,78 | soil |
| **PSU20** | 7,33 | 1,36 | 18,50 | 0,86 | plastics | 5,13 | 0,30 | 5,89 | 2,49 | soil |

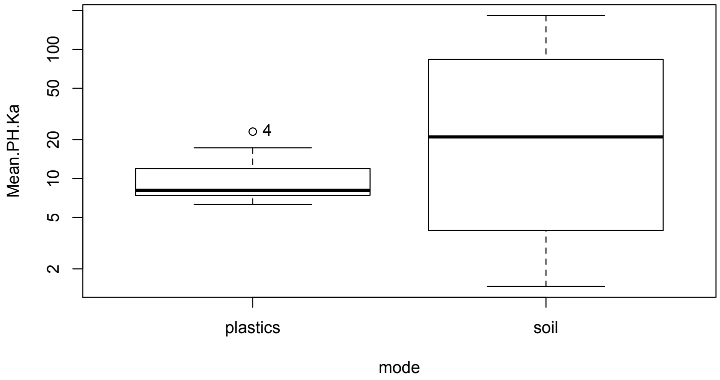

*Figure 11: Boxplots of PSUs measured in the plastic mode and in the soil mode.*

Figure 11 shows a boxplot of both measuring modes. The interquartile range of the soil mode results (78,2 cps) is much broader than the range to the plastic mode results (3,7 cps). The median value of the soil mode results (21 cps) is higher than the mean value of the plastic mode results (8,1 cps).

The correlation between the soil mode results and the plastic mode results is not clear, i.e. there is no conversion factor which can be used to determine the intensity from the soil mode by measuring with the plastics mode and vice versa.

Figure 12 shows the measured values for each PSU sample. In some cases (e.g. PSU1) the measured intensity in the soil mode is higher, in other cases (e.g. PSU3) the measured intensity in the plastics mode is higher. This case occurs at low intensities (maximum peak height < 25 cps). The following measurements were done using the soil mode because (I) all prior measurements at ABF were done in the soil mode, thus they can be compared and (II) the broader range of the results seems to be more practical for comparing the intensity of samples.

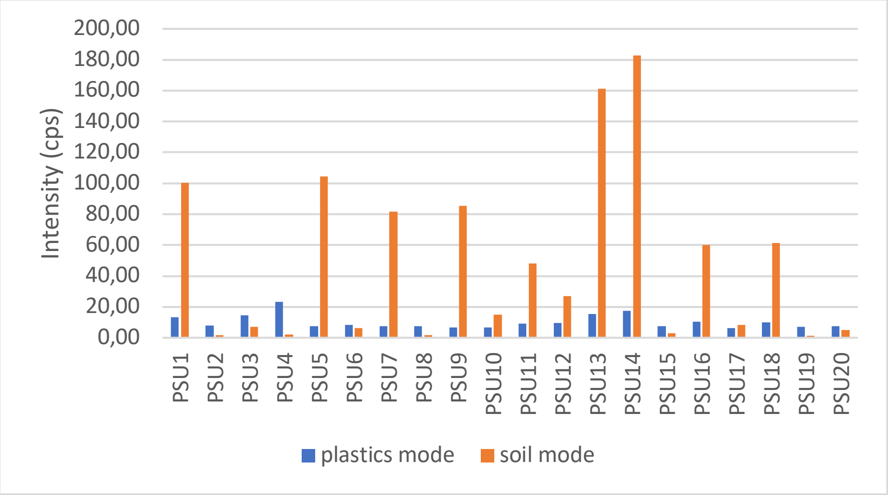

*Figure 12: Measured results of ka peak height of 20 PSU samples. Oranges bars show the results from soil mode; blue bars show the plastic mode results*

The plastics mode has a thickness correction which can be disabled or enabled by the user. This thickness correction was evaluated by measuring BAM-H010 with 3 different thicknesses. In this case, the thickness of the samples was known so this data could be entered into the XRF device setting. All three pellets have been measured in the plastics mode with an enabled and a disables thickness correction (tc). Additionally, the results from measuring in the soil mode were compared. Table 13 shows the results of these measurements. Column C shows the intensity of all measurements. As the thickness correction should minder the thickness as a source of error it can be seen that it has a low impact on the result. Still, the results from the 1 mm, the 2 mm, and the 6 mm samples differ. Thus, the thickness correction does not seem like a practical setting for eliminating the thickness as a source of error. Even with an enabled thickness correction mode, the plastics mode is not the preferable setting for the following analysis.

*Table 13: Results from measuring BAM-H010 in the plastics mode with an enabled or disabled thickness correction*

| Sample | Measuring Mode | Mean-PH-Ka | STD-PH-Ka | CV%-PH-Ka |
|---|---|---|---|---|
| **BAM-H010 1 mm** | Soil | 53,49 | 0,65 | 1,22 |
| **BAM-H010 1 mm** | Plastics without tc | 8,21 | 1,34 | 16,31 |
| **BAM-H010 1 mm** | Plastics with tc | 6,92 | 1,47 | 21,30 |
| **BAM-H010 2 mm** | Soil | 104,76 | 0,50 | 0,47 |
| **BAM-H010 2 mm** | Plastics without tc | 11,90 | 1,16 | 9,76 |
| **BAM-H010 2 mm** | Plastics with tc | 13,36 | 2,52 | 18,85 |
| **BAM-H010 6 mm** | Soil | 135,66 | 2,77 | 2,04 |
| **BAM-H010 6 mm** | Plastics without tc | 23,86 | 6,08 | 25,48 |
| **BAM-H010 6 mm** | Plastics with tc | 23,40 | 1,21 | 5,15 |

### 3.3.5 Sources of error - summary

Some potential sources of error could be determined as they are influencing the measuring results. Table 14 shows whether an evaluated potential source of error influences the measuring result or not.

*Table 14: Impacts of potential sources of error regarding research question 1*

| Source | Impact |
|---|---|
| Surface condition | ✓ |
| Sample Thickness | ✓ |
| Distribution | ✗ |
| Software | ✓ |

The surface structure of the sample has an impact on the measuring result. It plays a role whether the sample is granulated, pressed or in its “normal”, i.e. untreated condition. Raw samples show the highest intensity.

The sample thickness could also be identified as having an impact on the measuring result. Thinner samples show a lower intensity of bromine than thicker samples. The plastic type of the sample influences the slope of the conversion function. Different plastic categories lead to different correlations between the thickness and the measuring result. Thus, a conversion model to correct the measurement error due to the thickness of the sample is not available to date (or not known to the author). It has to be defined for every plastic type. A generic model for all common plastic types would not be representative.

The distribution was identified as not having an impact on the measuring results. It can be asserted that BFRs are attached to plastics homogenously. Thus, it does not matter on which spot of the sample the XRF analysis is executed.

The software calibration, however, does have an impact on the results. Measuring with the soil mode shows higher intensities than measuring with the plastics mode. The XRF software offers different measuring modes which use varying filters, leading to different results. A finding of this analysis was that there is no clear correlation between the plastics mode and the soil mode. Comparing results which were measured in the different modes appears difficult. Even qualitative conclusions differ from those measured with the soil mode. Thus, the further measurements were executed in the soil mode.

## 3.4 Quantities of bromine in selected product categories

Referring to the results from chapter 3.2, no quantitative analyses of the Br concentration have been made. Figure 13 shows the thickness of all samples in boxplots, sorted by product categories (the thickness of every sample is presented in the appendix). It can be seen that most of the samples are not thicker than 3 mm. The boxplots show that the group of mobile phones contained the thinnest subsamples. The subsamples of the residual devices have a median value of ca. 2,5 mm Thus, the measuring error due to the thickness is significant. For the following measurements no thickness correction has been applied, since there were no conversion models for all occurring plastic types available. Generating these models would have gone beyond the scope of this master's thesis.

But the measured intensity of the samples has still been compared. Although it has to be mentioned, that the samples are made of different plastic types. Thus, their measured intensities are not completely comparable.

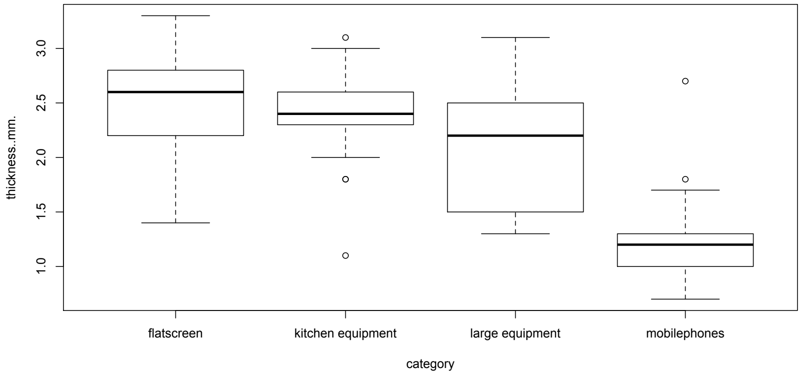

*Figure 13: Thickness of all samples in mm.*

Figure 14 shows the plastic types found in the samples per each product category. The bars do not represent the number of the samples, but the number of the plastics types found in the samples.

That is, if a sample is made out of ABS and PE both plastic categories are considered. 11 different plastic types have been found. In all analysed categories, ABS has been the main plastic type. In total, 125 samples have been analysed, whereof 80 contained ABS. That means, 64 % of all products contained ABS. The second most plastic type has been PC, which was found in 17 products (14 %), followed by PP, found in 16 products (13 %). The highest variation within a product category shows the group of mobile phones.

The high variation of plastic types makes a quantitative analysis of Br difficult since there is no correction model for every plastic type defined. Thus, this chapter concentrates on the qualitative analysis whether a sample is equipped with Br or not.

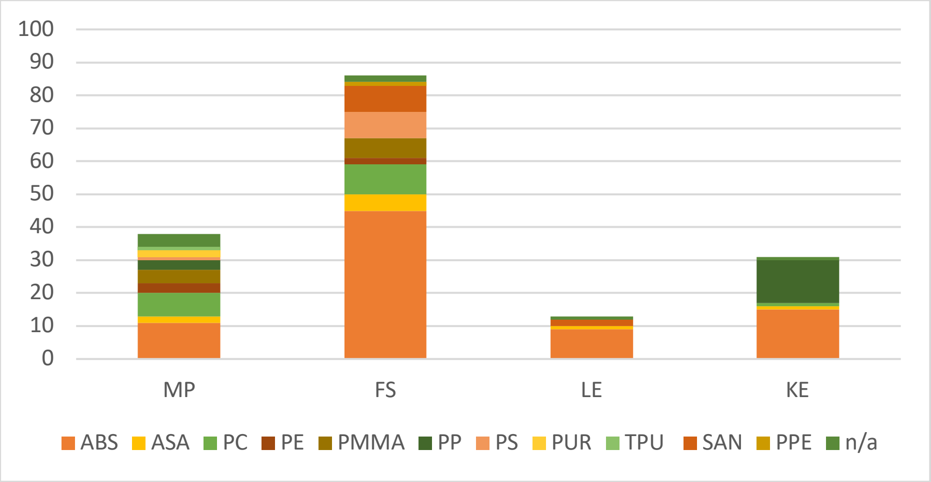

*Figure 14: Plastic categories per analysed product category, showing all plastic categories that have been detected in the analysed samples*

### 3.4.1 Bromine in mobile phones

40 cellular phones have been purchased, whereof 20 were “classical” phones (MPO) with a keypad and 20 were smartphones with a touchscreen (MPN). The “classical” phones were further defined as “old mobile phones”.

Some mobile phones could not be used for the analysis, because the housings were not made of plastics or the plastic housings could not be opened. Graphics 15 and 16 show a) a successful preparation of a mobile phone and b) an unsuccessful preparation due to a metal-plastic housing. At example a) the backside cover (red ring) was used for the subsamples which was the main spot for sample extraction at all mobile phones. At example b) it was not possible to part the metal from plastic. In this case, the housing could not be used for the analysis.

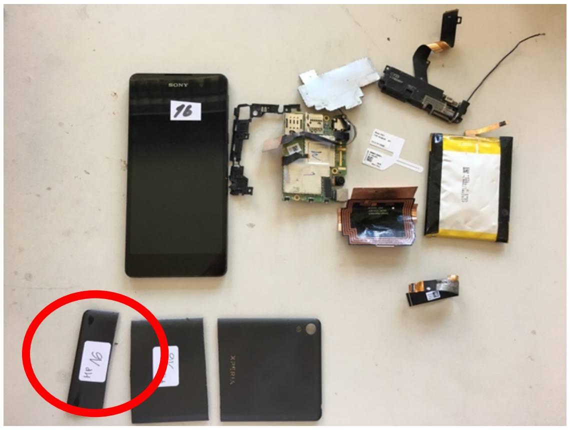

*Figure 15: example of the dismantling and subsample preparation process*

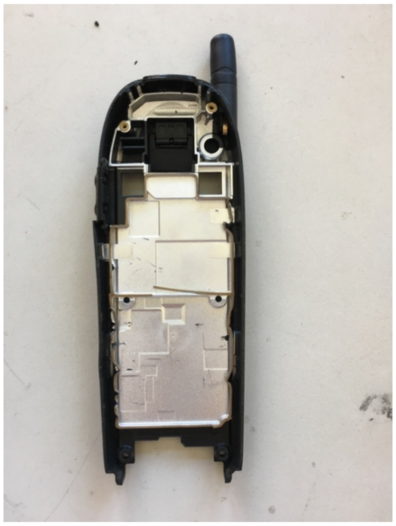

*Figure 16: Unsuccessful preparation of a sample due to a metal-plastic housing*

Thus, from 40 mobile phones 32 could be analysed, whereas 18 where old phones with a keyboard and 14 were smartphones. Table 15 shows the results of the old mobile phones. The 18 old phones were built between 1999 and 2010. 12 of these devices came on market prior the RoHS directive entered into force.

Only one sample, a Nokia 3510i built in 2002 had a ka/kb ratio > 6 (MP_O_7). This sample was made of ABS and built in 2002. It is noticeable that another sample from the same model but with a different colour did not contain Br (MP_O_6).

*Table 15: Results of old mobile phones*

| Tag | Brand | Model | Year of Production | Material | Colour | Ka peak Height | StD | Ka/Kb ratio |
|---|---|---|---|---|---|---|---|---|
| MP_O_1 | Bosch | 909 Dual | 1999 | ABS+PC | blue | 0,92 | 0,03 | 0,76 |
| MP_O_2 | Nokia | 8210 | 1999 | PC+ABS | blue | 0,94 | 0,03 | 0,80 |
| MP_O_3 | Nokia | 3310 | 2000 | PC+ABS | blue | 1,04 | 0,08 | 0,66 |
| MP_O_4 | Nokia | 3310 | 2000 | ASA | beige/multi | 1,49 | 0,12 | 0,73 |
| MP_O_5 | Samsung | R210 | 2001 | ABS | blue | 1,46 | 0,16 | 0,89 |
| MP_O_6 | Nokia | 3510i | 2002 | ABS | blue | 0,99 | 0,07 | 0,71 |
| MP_O_7 | Nokia | 3510i | 2002 | ABS | white | 62,14 | 1,02 | 6,18 |
| MP_O_8 | Nokia | 6310i | 2002 | PC+ABS | silver | 0,94 | 0,13 | 0,74 |
| MP_O_9 | Nokia | 6230 | 2004 | ABS | silver | 0,94 | 0,04 | 0,76 |
| MP_O_10 | Motorola | RAZR V3 | 2004 | n/a | black | 1,15 | 0,11 | 1,06 |
| MP_O_11 | Sony Ericsson | S700i | 2004 | ASA | silver | 0,98 | 0,15 | 0,76 |
| MP_O_12 | Motorola | V3i | 2005 | n/a | black | 2,36 | 0,19 | 1,71 |
| MP_O_13 | LG | KG320S | 2006 | PMMA | black | 0,82 | 0,11 | 0,87 |
| MP_O_14 | Sony Ericsson | K750i | 2006 | n/a | black | 0,73 | 0,04 | 0,87 |
| MP_O_15 | Sony Ericsson | K800i | 2006 | PMMA | silver | 1,05 | 0,03 | 0,78 |
| MP_O_16 | Sony Ericsson | W580i | 2007 | PMMA | white | 1,45 | 0,11 | 1,16 |
| MP_O_17 | Samsung | B2100 | 2009 | TPU | black | 1,64 | 0,07 | 0,50 |
| MP_O_18 | Samsung | GT-B2710 | 2010 | PUR | black | 1,18 | 0,04 | 0,69 |

Table 16 shows the results from new mobile phones, i.e. smart phones without a keypad which were built between 2008 and 2015. That means, all models have been built after the RoHS directive entered into force. No sample has been tested positive on bromine, although 7 different brands have been analysed. All samples comply with the RoHS directive in terms of contamination of brominated flame retardants.

*Table 16: Results of new mobile phones*

| Tag | Brand | Model | Year of Production | Material | Colour | Ka peak Height | StD | Ka/Kb ratio |
|---|---|---|---|---|---|---|---|---|
| MP_N_1 | Sony Xperia | Xperia | 2008 | PE | black | 0,89 | 0,15 | 0,83 |
| MP_N_2 | Samsung | S5230 Star | 2009 | PC+ABS | black | 0,95 | 0,09 | 0,86 |
| MP_N_3 | San Francisco | Orange | 2011 | PMMA | white | 0,99 | 0,10 | 0,62 |
| MP_N_4 | Nokia | Lumia 710 | 2011 | PC+ABS | white | 0,83 | 0,06 | 0,66 |
| MP_N_5 | LG | Optimus L7 P700 | 2012 | PP | white | 0,89 | 0,02 | 0,82 |
| MP_N_6 | LG | Optimus L7 P700 | 2012 | PE | white | 0,77 | 0,01 | 0,85 |
| MP_N_7 | Sony | Xperia S | 2012 | PE | black | 1,05 | 0,08 | 0,80 |
| MP_N_8 | Nokia | Lumia 520 | 2013 | n/a | black | 0,91 | 0,10 | 0,70 |
| MP_N_9 | LG | L Bello | 2014 | PC | black | 1,60 | 0,04 | 0,29 |
| MP_N_10 | Huawei | Ascend | 2014 | PP | black | 0,93 | 0,06 | 0,92 |
| MP_N_11 | Samsung | Galaxy J1 | 2015 | ABS | white | 0,78 | 0,08 | 0,78 |
| MP_N_12 | LG | Spirit | 2015 | PP | black | 1,04 | 0,05 | 0,86 |
| MP_N_13 | Huawei | P8 Lite | 2015 | PS | black | 0,72 | 0,03 | 0,86 |
| MP_N_14 | Wiko | Ridge 4G | 2015 | PUR | black | 0,92 | 0,02 | 0,75 |

Summing up all mobile phones, only 1 out of 32 units contained Br. All other devices have been tested negative on Br. In other words, ca. 3 % of all analysed mobile phones contained Br.

### 3.4.2 Bromine in large WEEE

Large WEEE is defined as products where the longest edge has to be equal to or larger than 50 cm. Thus, devices like washing machines, laundry dryers, dishwashers, refrigerators, etc. rank among large WEEE. The subsamples were taken from the covers on the top of the front side of the samples (5 washing machines and 5 dishwashing machines). Behind a transparent plastic cover the plastic housing of the electronic parts is installed. Subsamples were extracted from this housing. Figure 17 shows the extraction of a subsample (LE_6).

*Figure 17: Extraction of a subsample from large equipment*

*Table 17: Results of large equipment*

| Tag | Brand | Model | Material | Notes | colour | Mean-PH-Ka | STD-PH-Ka | Mean-Ka/Kb |
|---|---|---|---|---|---|---|---|---|
| LE_1 | Indesit | IWE8168 | ABS | WM | white | 1,00 | 0,04 | 0,83 |
| LE_2 | Bauknecht | IK Care 6B | ASA+ABS | WM | white | 0,99 | 0,09 | 0,70 |
| LE_3 | AEG | n/a | ABS | DW | black | 1,38 | 0,05 | 0,62 |
| LE_4 | Privileg | Basic 76 | ABS | WM | white | 1,13 | 0,02 | 0,69 |
| LE_5 | Miele | G647 | ABS | DW | white | 1,35 | 0,22 | 0,77 |
| LE_6 | Miele | G676 | ABS | DW | white | 1,28 | 0,05 | 0,72 |
| LE_7 | Zanussi | ZDTS 101 | ABS+SAN | DW | silver | 1,35 | 0,08 | 0,67 |
| LE_8 | Whirlpool | n/a | ABS+SAN | WM | white | 1,17 | 0,02 | 0,68 |
| LE_9 | AEG | GS60AIB | n/a | DW | black | 0,99 | 0,12 | 0,64 |
| LE_10 | Siemens | Wash & Dry 1220 | ABS | WM | white | 0,91 | 0,08 | 0,70 |

Table 17 shows the results from analysing the large WEEE. The column “Notes” shows the subcategory of the sample (WM = washing machine, DW = dishwashing machine). There was no data on the year of production of the devices available. Thus, it cannot be evaluated whether all samples were built after or before the RoHS directive entered into force. 9 out of 10 devices contained ABS, the plastic type of one sample (LE_9) could not be identified.

All analysed samples were Br-free. The reason for the negative Br results might indicate that there was no reason to add BFRs due to a low possibility of heat dissipation. Thus, the product category “large equipment” seems to be useful for plastic recycling due to its Br-free characteristics.

### 3.4.3 Bromine in flat screens

Flat screen housings are typically made of components from different materials, i.e. the front cover is made of a different plastic type than the back cover. Thus, these parts have been analysed separately. Some products came with a separate stand. Since stands were not defined as part of the housing, they were not object of evaluation. Only two collected flat screens could not get dismantled. The rest, 27 flat screens (front side and back side), were dismantled and subsequently analysed.

Table 18 shows the results from analysing the front sides of the screens. Four samples show a significant amount of Br (6, 9, 21, 25). Noticeable is sample FS_FS25, a Samsung flat screen built in 2005, which shows an intensity of Br of ca. 3090 cps. 2 samples which were positive on Br were built after the RoHS directive entered into law, FS_FS9 and FS_FS21. Again, it is not comprehensible, in which country these samples were purchased. It might be possible that they were bought in countries which did not ratify the Stockholm Convention, respectively do not have to follow the RoHS directive (no EU member).

There were some samples, nr. 2, 13 and 20, which showed some intensity of Br but did not have a ka/kb ratio of more than 6, which would be the indicator for Br appearance. Thus, these samples are not coloured blue in this table.

Table 19 shows the results from analysing the backsides of the screens. 7 samples show a significant amount of bromine: Nr. 2, 3, 4, 5, 6, 9 and 18. 5 of these samples were built after the RoHS directive entered into force, the year of production of sample nr. 6 could not be identified.

It is noticeable that some samples were only positive regarding Br on the frontside and some only at the backside. Therefore, the separation of frontside and backside proved itself as meaningful for the analysis. The fact that more backsides contained Br than front sides might be due to the closeness to the electric compounds at the backside.

*Table 18: Results of flat screen front sides*

| Tag | Manufacturer | Model | Year of production | Material Frontside ATR | colour | Mean-PH-Ka | STD-PH-Ka | Mean-Ka/Kb |
|---|---|---|---|---|---|---|---|---|
| FS_FS1 | Acer | AL712 | 2003 | ABS+PC | beige | 1,47 | 0,05 | 0,65 |
| FS_FS2 | Benq | T705 | 2008 | ABS | silver | 10,63 | 0,29 | 4,31 |
| FS_FS3 | HP | LI700 | 2003 | PMMA | silver | 1,95 | 0,02 | 0,85 |
| FS_FS4 | Samsung | 943BM | 2008 | ABS | silver | 1,26 | 0,14 | 0,70 |
| FS_FS5 | Samsung | B2240BM | 2011 | ABS | black | 1,52 | 0,03 | 0,66 |
| FS_FS6 | Belinea | 1730S1 | n/a | PMMA | silver | 192,52 | 2,74 | 6,93 |
| FS_FS7 | Samsung | 226BW | 2007 | ABS | black | 1,86 | 0,07 | 0,73 |
| FS_FS8 | Samsung | 524B420BW | 2013 | ABS+SAN | black | 1,22 | 0,02 | 0,61 |
| FS_FS9 | Asus | VS228 | 2015 | ABS HIPS | black | 94,01 | 2,00 | 6,15 |
| FS_FS10 | Asus | VK222 | 2009 | ASA | black | 1,57 | 0,04 | 0,71 |
| FS_FS11 | Dell | 1702FP | 2008 | PC+ABS | grey | 1,46 | 0,07 | 0,64 |
| FS_FS12 | Fujitsu Siemens | C17-2 | 2005 | PC+ABS | silver | 1,34 | 0,04 | 0,68 |
| FS_FS13 | HP | D5064 | 2002 | ASA+SAN+ABS | beige | 51,75 | 0,21 | 5,53 |
| FS_FS14 | Samsung | 1515 | 2002 | ABS | silver | 1,53 | 0,09 | 0,64 |
| FS_FS15 | Acer | AL506 | 2005 | ABS+ASA | beige | 1,30 | 0,21 | 0,73 |
| FS_FS16 | HP | 20555SH249 | 2007 | ABS+PC | silver | 1,18 | 0,01 | 0,67 |
| FS_FS17 | Media | MD5042OC | 2002 | PMMA+ABS | silver | 1,60 | 0,05 | 0,65 |
| FS_FS18 | HP | P9621D | 2015 | PMMA+ABS | silver | 1,52 | 0,10 | 0,62 |
| FS_FS19 | Benq | Q9T5 | 2007 | ABS | beige | 1,39 | 0,10 | 0,64 |
| FS_FS20 | Iiyama | ProLite 38a | 2002 | HIPS | beige | 25,86 | 1,02 | 4,74 |
| FS_FS21 | Philips | 190P6 | 2006 | PC+ABS | silver | 739,75 | 15,31 | 6,72 |
| FS_FS22 | Meditec | SHB-1756 | 2006 | PMMA | black | 1,67 | 0,06 | 0,58 |
| FS_FS23 | Acer | AL1721 | 2003 | ABS+SAN | grey | 2,30 | 0,05 | 1,00 |
| FS_FS24 | Benq | FP93G | 2007 | PE+PC+ABS | silver | 1,64 | 0,04 | 0,67 |
| FS_FS25 | Samsung | 713BM5 | 2005 | PMMA+ABS | silver | 3.092,84 | 43,49 | 6,13 |
| FS_FS26 | HP | 20555 | 2007 | ABS | silver | 1,20 | 0,05 | 0,63 |
| FS_FS27 | Gericom | 51702D | n/a | PE+PC+ABS | silver | 1,79 | 0,20 | 0,68 |

*Table 19: Results of flat screen back sides*

| Tag | Manufacturer | Model | Year of production | Material Backside ATR | colour | Mean-PH-Ka | STD-PH-Ka | Mean-Ka/Kb |
|---|---|---|---|---|---|---|---|---|
| FS_BS1 | Acer | AL712 | 2003 | ABS+PC | beige | 1,26 | 0,06 | 0,57 |
| FS_BS2 | Benq | T705 | 2008 | ABS | black | 548,59 | 2,82 | 6,99 |
| FS_BS3 | HP | LI700 | 2003 | PS | black | 1.425,51 | 4,80 | 6,79 |
| FS_BS4 | Samsung | 943BM | 2008 | ABS+HIPS | black | 1.420,58 | 14,59 | 6,86 |
| FS_BS5 | Samsung | B2240BM | 2011 | HIPS+ABS | black | 65,18 | 1,27 | 6,01 |
| FS_BS6 | Belinea | 1730S1 | n/a | ABS | black | 112,67 | 0,83 | 6,43 |
| FS_BS7 | Samsung | 226BW | 2007 | ABS+HIPS | black | 1,54 | 0,09 | 0,68 |
| FS_BS8 | Samsung | 524B420BW | 2013 | HIPS+ABS | black | 41,96 | 0,74 | 5,81 |
| FS_BS9 | Asus | VS228 | 2015 | ABS | black | 61,91 | 0,58 | 6,03 |
| FS_BS10 | Asus | VK222 | 2009 | ABS+SAN | black | 1,31 | 0,04 | 0,62 |
| FS_BS11 | Dell | 1702FP | 2008 | ABS+PC | black | 1,38 | 0,07 | 0,61 |
| FS_BS12 | Fujitsu Siemens | C17-2 | 2005 | n/a | grey | 1,40 | 0,04 | 0,71 |
| FS_BS13 | HP | D5064 | 2002 | ABS+SAN | black | 51,77 | 1,11 | 5,73 |
| FS_BS14 | Samsung | 1515 | 2002 | ABS | black | 1,57 | 0,21 | 0,57 |
| FS_BS15 | Acer | AL506 | 2005 | ABS | beige | 1,30 | 0,17 | 0,65 |
| FS_BS16 | HP | 20555SH249 | 2007 | ABS | black | 4,43 | 0,27 | 2,66 |
| FS_BS17 | Media | MD5042OC | 2002 | ABS+HIPS | grey | 8,99 | 0,19 | 3,70 |
| FS_BS18 | HP | P9621D | 2015 | ABS+SAN | black | 123,88 | 0,53 | 6,60 |
| FS_BS19 | Benq | Q9T5 | 2007 | ASA+ABS | black | 5,50 | 0,23 | 2,56 |
| FS_BS20 | Iiyama | ProLite 38a | 2002 | PPE+HIPS | beige | 1,51 | 0,06 | 0,76 |
| FS_BS21 | Philips | 190P6 | 2006 | n/a | grey | 14,61 | 0,26 | 3,82 |
| FS_BS22 | Meditec | SHB-1756 | 2006 | ASA+ABS | beige | 1,44 | 0,07 | 0,62 |
| FS_BS23 | Acer | AL1721 | 2003 | ABS | beige | 2,03 | 0,11 | 0,87 |
| FS_BS24 | Benq | FP93G | 2007 | ABS+SAN | black | 12,74 | 0,88 | 4,07 |
| FS_BS25 | Samsung | 713BM5 | 2005 | ABS | black | 1,48 | 0,08 | 0,51 |
| FS_BS26 | HP | 20555 | 2007 | ABS+SAN | black | 11,13 | 0,60 | 4,42 |
| FS_BS27 | Gericom | 51702D | n/a | ABS | black | 1,74 | 0,15 | 0,67 |

Figure 18 shows the ka/kb ratios of all measured flat screens, at which the front covers are contrasted with the back covers. Looking at sample nr. 6, both sides show a ratio > 6. But there are some samples which show a Br content only in one of the two housing parts.

4 out of 27 front side covers were equipped with Br and 7 out of 27 backside covers were equipped with Br. 9 flatscreens out of 27 contained at least one component containg Br of the analysed flat screen housings were equipped with Br. Table 20 summarizes all brominated flat screens without considering whether the front side or the backside contains bromine.

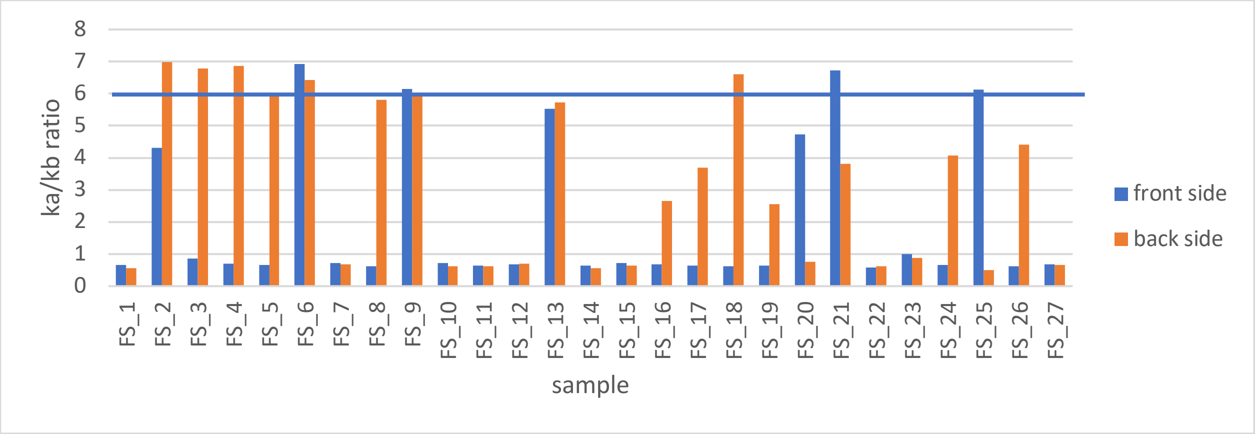

*Figure 18: Bar chart of the ka/kb ratios of every flat screen. Blue bars show the results from front sides, orange bars show those of the back sides*

*Table 20: Summary of all brominated flat screens. Considering the front sides and the back sides, 8 flat screen samples contained bromine. Column „material ATR“ shows the materials of the front side and the back side, column “colour” shows the colour of the front side and the back side. Column „Mean ph-ka“ shows the highest measured Br intensity within the sample (front side or back side).*

| Tag | Manufacturer | Model | Year of production | Material ATR | colour | Mean-PH-Ka |
|---|---|---|---|---|---|---|
| FS_2 | Benq | T705 | 2008 | ABS | Black/silver | 548,59 |
| FS_3 | HP | LI700 | 2003 | PS/PMMA | Black/silver | 1.425,51 |
| FS_4 | Samsung | 943BM | 2008 | ABS+HIPS/ABS | Black/silver | 1.420,58 |
| FS_5 | Samsung | B2240BM | 2011 | HIPS+ABS/ABS | Black/black | 65,18 |
| FS_6 | Belinea | 1730S1 | n/a | ABS/PMMA | Black/silver | 192,52 |
| FS_9 | Asus | VS228 | 2015 | ABS/ABS+HIPS | Black/black | 94,01 |
| FS_18 | Benq | T705 | 2008 | ABS+SAN/PMMA+ABS | Black(silver | 548,59 |
| FS_21 | Philips | 190P6 | 2006 | PC+ABS/n/a | Silver/grey | 739,75 |
| FS_25 | Samsung | 713BM5 | 2005 | PMMA+ABS/ABS | Silver/black | 3.092,84 |

### 3.4.4 Bromine in kitchen equipment

This product category was the most heterogenous, due to its multiple subcategories. The following categories were under evaluation (table 21).

Due to the fact that all samples were not tagged with the exact product name or serial number, the year of production could not be determined.

Table 22 shows the results. One device, KE_6, a mixer, was equipped with Br. Sample nr. 5 and 18 did also show some Br intensity but both did not fulfil the ka/kb ratio > 6.

Thus, 1 sample of the kitchen equipment samples were equipped with Br. The positive tested product was a mixer made of ABS. Another mixer, produced by the same brand, did not show a bromine content (KE_5), although its ka/kb ratio almost overstepped the benchmark of 6

*Table 21: Subcategories of kitchen equipment samples and the number of samples per subcategory.*

| **Subcategory** | **Abbreviation** | **Number of samples** |
|---|---|---|
| Kettle | K | 6 |
| Mixer | MX | 4 |
| Coffee Machine | CM | 6 |
| Cutter | CU | 1 |
| Toaster | T | 8 |
| Stick Blender | SB | 3 |
| Juice Extractor | JE | 1 |
| total | | 29 |

*Table 22: Results of kitchen equipment*

| Tag | Subcategory | Brand | Material | Color | Mean-PH-Ka | STD-PH-Ka | Mean-Ka/Kb |
|---|---|---|---|---|---|---|---|
| KE_1 | WK | Siemens | n/a | white | 0,77 | 0,09 | 0,78 |
| KE_2 | WK | TCM | PP | white | 1,27 | 0,14 | 0,60 |
| KE_3 | WK | SimPexBasic | PP | black | 1,41 | 0,07 | 0,68 |
| KE_4 | SB | Moulinex | ABS | white | 1,27 | 0,04 | 0,58 |
| KE_5 | MX | Moulinex | ABS | white | 19,09 | 0,20 | 5,18 |
| KE_6 | MX | Moulinex | ABS | black | 397,97 | 6,69 | 6,69 |
| KE_7 | MX | Ciatronic | ABS+ASA | white | 1,62 | 0,08 | 0,53 |
| KE_8 | T | Kenwood | PP | white | 1,27 | 0,15 | 0,73 |
| KE_9 | T | Severin EG | PP | white | 1,19 | 0,04 | 0,60 |
| KE_10 | T | Lutter+Parter Studio | PP | white | 1,24 | 0,05 | 0,65 |
| KE_11 | T | Lutter+Parter Studio | PP | grey | 1,20 | 0,08 | 0,64 |
| KE_12 | T | Russell Hobbs | PP | black | 1,61 | 0,14 | 0,69 |
| KE_13 | T | Bosch | PP | black | 1,36 | 0,06 | 0,68 |
| KE_14 | T | TCM | PP | blue | 1,27 | 0,06 | 0,65 |
| KE_15 | KM | Bosch | ABS | white | 1,27 | 0,06 | 0,53 |
| KE_16 | WK | Severin EG | PP | white | 1,39 | 0,13 | 0,64 |
| KE_17 | MX | Trion | ABS | white | 1,39 | 0,13 | 0,68 |
| KE_18 | T | Maltatech | PP | black | 32,15 | 0,20 | 4,18 |
| KE_19 | WK | Severin EG | PP | white | 1,18 | 0,11 | 0,71 |
| KE_20 | SMX | Moulinex | ABS | white | 1,36 | 0,01 | 0,74 |
| KE_21 | SMX | ESGE | ABS | white | 1,30 | 0,07 | 0,66 |
| KE_22 | KM | Superespresso | ABS | grey | 1,35 | 0,05 | 0,39 |
| KE_23 | KM | Nespresso | ABS | black | 1,63 | 0,15 | 0,69 |
| KE_24 | JE | AEG | ABS | n/a | 1,19 | 0,05 | 0,73 |
| KE_25 | CU | Kenwood | ABS | n/a | 1,42 | 0,11 | 0,56 |
| KE_26 | WK | TCM | PP | white | 1,21 | 0,04 | 0,60 |
| KE_27 | KM | Nespresso | ABS | red | 1,78 | 0,11 | 0,67 |
| KE_28 | KM | Nespresso | ABS | black | 1,37 | 0,08 | 0,59 |
| KE_29 | KM | Nespresso | ABS+PC | black | 1,49 | 0,09 | 0,62 |

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### 3.4.5 Results

Figure 19 show the intensity (cps) from all evaluated categories. The vertical axis has a logarithmic scale. 9 flat screens (4 back sides, 7 front sides), 1 kitchen equipment and 1 old mobile phone contained Br, in sum 11 samples contained Br. It is remarkable, that the group of flat screens has the most products with a contamination of Br. Large Equipment and new mobile phones (smartphones) did not show a ka/kb ratio >6. The mean value of the Br intensity over all samples is 67.41 cps. Table 23 shows the number of brominated samples, compared to the total number of analysed samples.

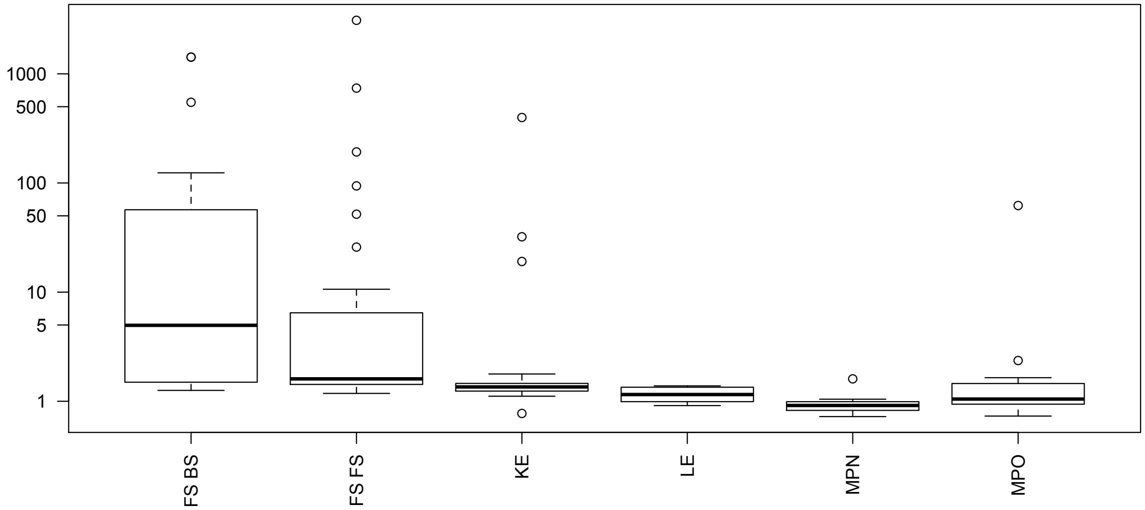

*Figure 19: Boxplots of Br intensity of all analysed product categories*

*Table 23: Number of total samples compared to the number of brominated samples*

| | Total number of samples | number of brominated samples |
|---|---|---|
| Mobile phones | 32 | 1 |
| Large equipment | 10 | 0 |
| Flat screens | 27 | 9 |
| Kitchen equipment | 29 | 1 |
| total | 98 | 11 |

4 samples of all products which contained Br were made of ABS, 10 samples were made of ABS or a combination of ABS and another plastic type. Figure 20 shows the appearance of plastic types in all Br plastics, considering the division in flat screen front sides and back sides. The plastic type as an impact on whether the sample contains Br or not has been tested with an ANOVA. The null hypothesis that the plastic type has no significant impact

could be accepted (p-value = 0,01). Thus, it can be stated that the plastic type of the sample does not imply whether this sample contains Br or not.

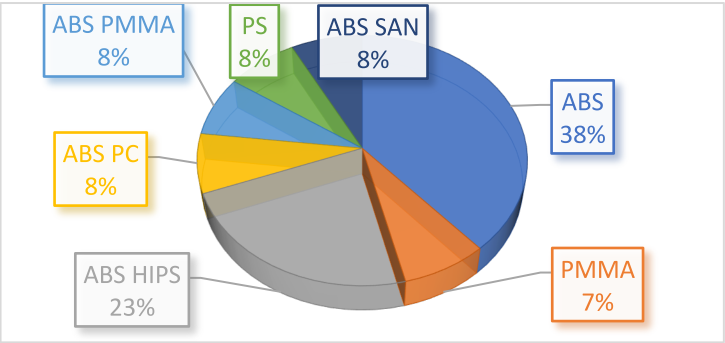

*Figure 20: Relative share of plastic types regarding all Br containing samples. About 38 % of the samples which contained Br were made of ABS, 84,6 % of them were made of ABS or a combination of ABS and another plastic type.*

The year of production of many samples could not be identified. However, figure 21 shows all samples from which it was known. It can be seen, that the sum of products which showed a ka/kb ratio > 6 decreased after 2005. But still, the analysis identified some products from 2015 which were equipped with Br.

The intensity of the samples is not simply comparable while it is influenced by other factors, e.g. the plastic type and the sample thickness. However, figure 22 shows the measured intensities (peak heights of ka) of all samples. The y-axis shows the ka/kb ratio. It can be seen that most of the analysed samples showed a ka/kb ratio of ca. 1, thus they were not equipped with Br. All samples with a ka/kb ratio > 6, i.e. all samples which contained bromine, showed an intensity of min. 90 cps.

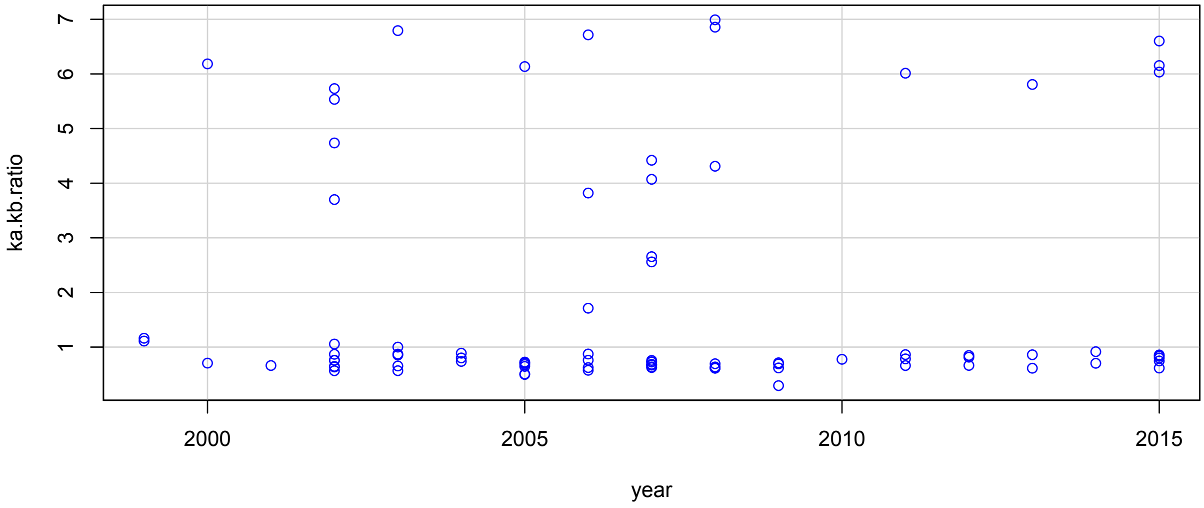

*Figure 21: Dot plot of all analysed samples categorized by year. The y-axis shows the ka/kb ratio.*

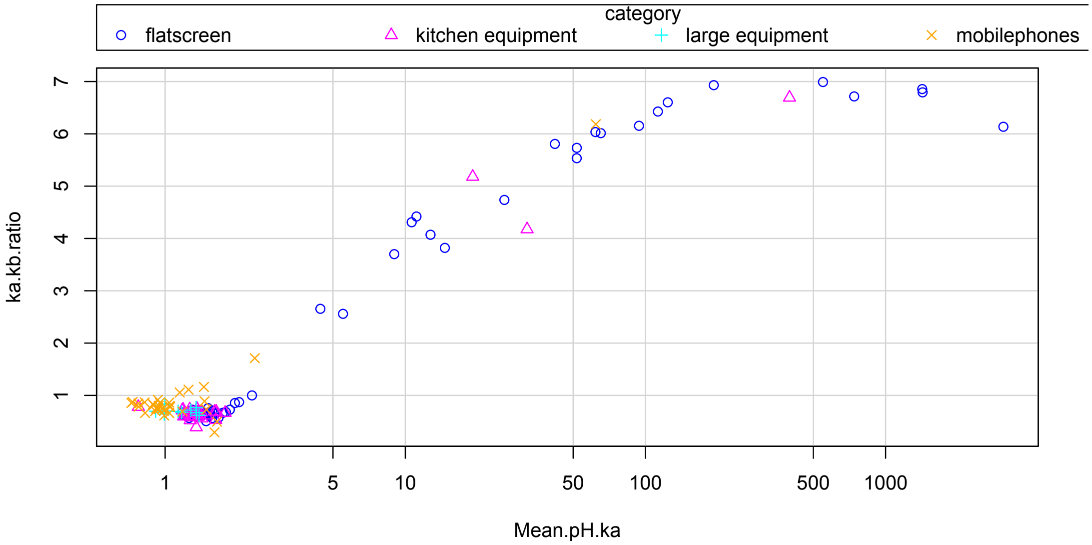

*Figure 22: Overview over all samples tagged by product category. The x-axis shows the mean peak height of ka (cps) with an exponential scale, the y-axis shows the ka/kb ratio.*

# 4 Discussion

Since brominated flame retardants have been identified as risky substances for human health and the environment, they were more and more substituted by other flame retardants whose impacts on health and environment have not been identified as risky so far. But still there is research missing on their effects. At least since legal regulations on brominated flame retardants popped up worldwide and especially in the European Union, brominated flame retardants faded out in the consumer market. But still, there are some products afloat, which contain Br. For example, in our samples we found one flat screen which was built in 2015 and contained BFR. Depending on the product category, even BFR equipped products are in use which were build prior the legal regulations on Br.

While recycling rates are getting lifted from time to time and on the other side, threshold limits for BFRs in consumer products are put down it is becoming more and more important to know whether a product is equipped with BFRs or not. The concentration of Br within a plastic part is critical for the decision whether it will be recycled or not.

Having a look on the analysis to identify the surface condition as a source of error, it has to be mentioned that the milling process exposed the analysed samples to temperatures which, in some cases, led to a melting process (see appendix). Although, dry ice has been added, the heating process could not be fully eliminated. Thus, the Br might have been decomposed. This might have led to a lower measured Br intensity within the granulate and the pellet. However, the surface condition could be determined as an impact factor on the measuring result, although the intensity of this impact was not analysed within this master’s thesis. It might be interesting for future studies to develop a correlation factor between the surface condition and the measuring result.

The pressed pellets had different stabilities due to their chemical structure. This circumstance might have had an effect on the measurement. Pressing under higher temperatures to soften the material could be useful to increase the stability in prospective analyses. Another way would be an addition of binder, e.g. cellulose, to the granulate (Haschke and Flock, 2017). In this paper, none of these methods have been aimed.

However, one main finding of these thesis is that the plastic category and the thickness of the sample play a critical role for calculating the Br concentration by using the measured Br intensity, i.e. the maximum peak height in cps. At ca. 7 mm a plateau of the measured intensity is reached. That is, at a certain point, the impact of the sample thickness on the measuring result is negligible. Most samples have a thickness of ca. 1-3mm. Thus, this attribute has to be considered when measuring their bromine concentration. Two possible ways to counter this fact may be effective. Firstly, a conversional model could be determined for every plastic type. Secondly, all samples could be granulated and pressed prior the XRF analysis. In the second case, the loss of bromine through the granulating process has to be considered.

Although, no predications on the Br concentration of the samples could be made, there are still some practical statements possible. Every product which shows a ka/kb ratio above 6 is equipped with bromine. The measured intensity of bromine is always a lower number than the Br concentration of the sample. E.g., a sample with 100 cps of Br has a concentration of at least 100 ppm (Aldrian et al., 2015). Thus, a sample with 1000 cps has a Br concentration of min. 1000 ppm. Correspondingly, statements regarding legal threshold limits can be made. Because such statements are still very unprecise, they have not been considered within this study.

The XRF is used to measure the BFR concentration indirectly. The legal limits are set for BFR substances and not for Br. Thus, a sample might be identified as having a BFR concentration above the limits, although it is equipped with PBDE lower than the allowed max. concentration and with HBCD lower than the allowed max. concentration. This should be considered in future research.

There might be products which contain Br, because their plastic parts come from recycled products which were equipped with brominated flame retardants. In this paper, no correlation could be determined. Further research is needed to analyse whether recycling of BFR plastics may lead to a contamination above the threshold limits.

In some samples, low intensities of Br have been measured. Further research is recommended, on how low concentrations of Br are toxic for humans and the environment. This may also be interesting for future legal regulations on brominated flame retardants.

# 6 Conclusion

Although measuring brominated flame retardants in WEEE plastics by using XRF spectroscopy is a useful method, some sources of error have to be considered. The surface condition and the thickness of the sample could be identified as influencing the results, as well as the used software mode (plastic or soil) and the plastic type of the sample. Within this paper many steps forward were done to evaluate XRF as a measuring technique for identifying Br in WEEE. But still, there is some research needed to build more exact models for a quantification of the Br concentration.

Second aim of this master's thesis was to analyse the content of brominated flame retardants in certain WEEE product categories. Some product categories are more suitable for recycling due to their low Br occurrence than others. Because the legal situations on WEEE recycling on the one hand and BFR in EEE on the other hand are prospected to change in the following years, it is important to monitor the Br concentrations of WEEE over time.

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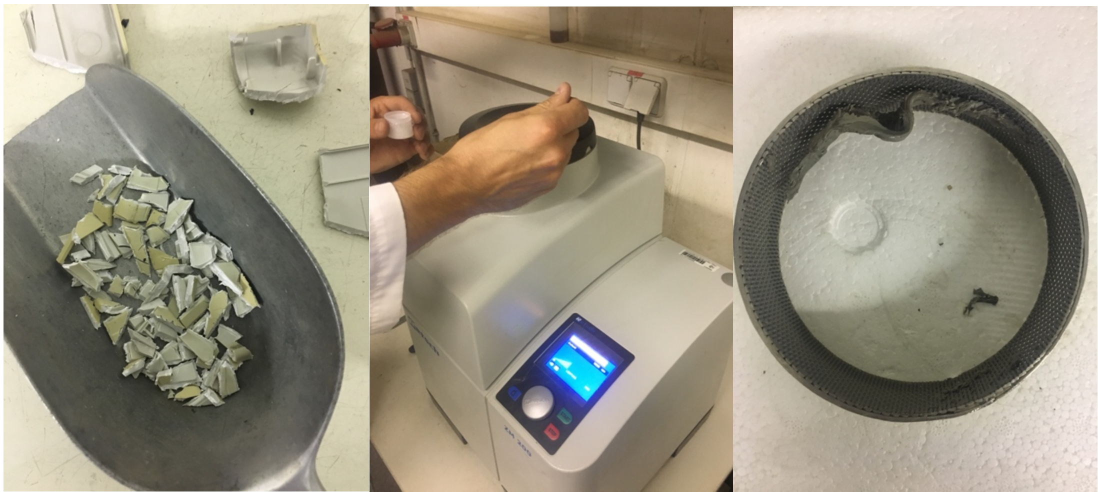
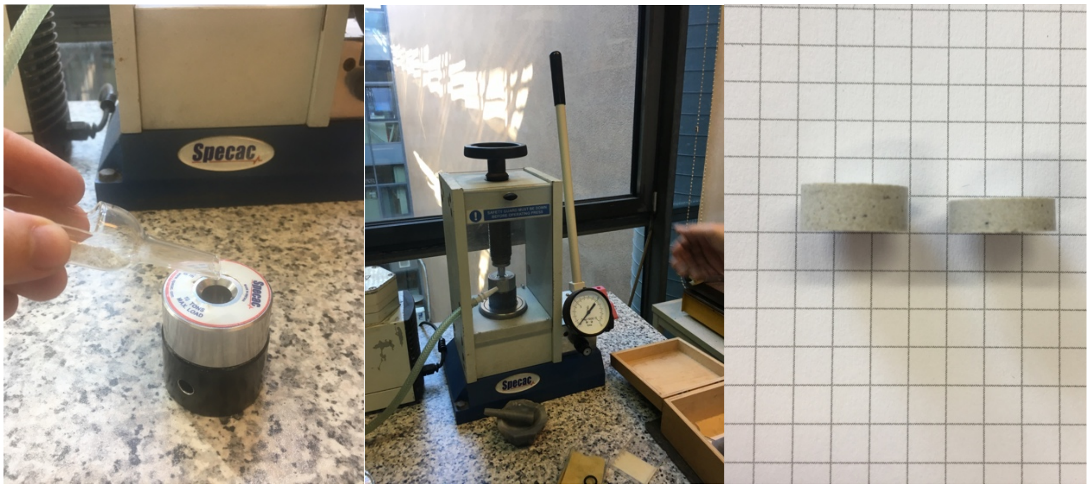
# Appendix



*Granulating procedure: (I) cut flat screen sample; (II) Pouring the sample in the centrifugal mill, milling; (III) distance sieve with melted flat screen sample (on the top of the image)*



*Pressing procedure: (I) Pouring the granulated sample in the pressing cylinder; (II) Pressing the granulate; (III) pressed pellets*

*New Mobile Phones complete table*

| category | Sample | subcategory | brand | model | year | Mean pH ka | std ph ka | cv% ph ka | ka/kb ratio | plastic type | color | thickness (mm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mobilephones | MP_N_01 | mobile phone new | Sony Xperia | Xperia | 2008 | 0,991641 | 0,099598 | 10,043775 | 0,615317 | PE | black | 1,2 |
| mobilephones | MP_N_02 | mobile phone new | Samsung | S5230 Star | 2009 | 1,604917 | 0,041777 | 2,60308 | 0,294208 | PC+ABS | black | 1,1 |
| mobilephones | MP_N_03 | mobile phone new | San Francisco | Orange | 2011 | 0,77573 | 0,080128 | 10,329419 | 0,784434 | PMMA | white | 0,8 |
| mobilephones | MP_N_04 | mobile phone new | Nokia | Lumia 710 | 2011 | 1,039519 | 0,049599 | 4,771385 | 0,861998 | PC+ABS | white | 1,1 |
| mobilephones | MP_N_05 | mobile phone new | LG | Optimus L7 P700 | 2012 | 0,894665 | 0,015559 | 1,739129 | 0,815129 | PP | white | 1,1 |
| mobilephones | MP_N_06 | mobile phone new | LG | Optimus L7 P700 | 2012 | 0,773805 | 0,012865 | 1,662603 | 0,846178 | PE | white | 1,1 |
| mobilephones | MP_N_07 | mobile phone new | Sony | Xperia S | 2012 | 0,825119 | 0,055605 | 6,73902 | 0,664176 | PE | black | 1,6 |
| mobilephones | MP_N_08 | mobile phone new | Nokia | Lumia 520 | 2013 | 0,950413 | 0,094889 | 9,984004 | 0,859566 | n/a | black | 1 |
| mobilephones | MP_N_09 | mobile phone new | LG | L Bello | 2014 | 0,910362 | 0,102678 | 11,27879 | 0,703582 | PC | black | 1,2 |
| mobilephones | MP_N_10 | mobile phone new | Huawei | Ascend | 2014 | 0,932641 | 0,06238 | 6,688539 | 0,915876 | PP | black | 1 |
| mobilephones | MP_N_11 | mobile phone new | Samsung | Galaxy J1 | 2015 | 0,723895 | 0,031103 | 4,296575 | 0,855883 | ABS | white | 0,7 |
| mobilephones | MP_N_14 | mobile phone new | LG | Spirit | 2015 | 0,920158 | 0,016392 | 1,781442 | 0,746584 | PP | black | 1 |
| mobilephones | MP_N_15 | mobile phone new | Huawei | P8 Lite | 2015 | 1,045122 | 0,079452 | 7,602133 | 0,800019 | PS | black | 1,3 |
| mobilephones | MP_N_16 | mobile phone new | Wiko | Ridge 4G | 2015 | 0,889726 | 0,152703 | 17,162871 | 0,832292 | PUR | black | 1 |

*New Mobile Phones complete table*

| category | Sample | subcategory | brand | model | year | Mean pH ka | std ph ka | cv% ph ka | ka/kb ratio | plastic type | color | thickness (mm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| mobilephones | MP_O_01 | mobile phone old | Motorola | SLVR L72 | 2007 | 0,919613 | 0,027762 | 3,018903 | 0,755878 | n/a | black | 0,8 |
| mobilephones | MP_O_03 | mobile phone old | Bosch | 909 Dual | 1999 | 1,251858 | 0,166073 | 13,266148 | 1,110197 | ABS+PC | blue | 1,1 |
| mobilephones | MP_O_04 | mobile phone old | Nokia | 8210 | 1999 | 1,450027 | 0,107637 | 7,42308 | 1,161694 | PMMA | white | 1,2 |
| mobilephones | MP_O_05 | mobile phone old | Nokia | 3310 | 2000 | 0,989752 | 0,069045 | 6,976019 | 0,706807 | ABS | blue | 1,3 |
| mobilephones | MP_O_06 | mobile phone old | Nokia | 3310 | 2000 | 62,141038 | 1,018588 | 1,639154 | 6,184035 | ABS | white | 1,3 |
| mobilephones | MP_O_07 | mobile phone old | Samsung | R210 | 2001 | 1,040362 | 0,079839 | 7,674176 | 0,662505 | PC+ABS | blue | 1,5 |
| mobilephones | MP_O_08 | mobile phone old | Nokia | 3510i | 2002 | 0,935722 | 0,042423 | 4,533706 | 0,759292 | ABS | silver | 1,2 |
| mobilephones | MP_O_09 | mobile phone old | Nokia | 3510i | 2002 | 0,821694 | 0,10664 | 12,978127 | 0,868268 | PMMA | black | 1,5 |
| mobilephones | MP_O_10 | mobile phone old | Nokia | 6310i | 2002 | 1,15009 | 0,106429 | 9,253971 | 1,055707 | n/a | black | 1,2 |
| mobilephones | MP_O_11 | mobile phone old | Nokia | 6230 | 2004 | 0,940913 | 0,132201 | 14,050326 | 0,737581 | PC+ABS | silver | 1,2 |
| mobilephones | MP_O_12 | mobile phone old | Motorola | RAZR V3 | 2004 | 0,940197 | 0,028592 | 3,041111 | 0,801417 | PC+ABS | blue | 1 |
| mobilephones | MP_O_13 | mobile phone old | Sony Ericsson | S700i | 2004 | 1,459184 | 0,164197 | 11,25265 | 0,888337 | ABS | blue | 1 |
| mobilephones | MP_O_14 | mobile phone old | Motorola | V3i | 2005 | 1,644815 | 0,070428 | 4,281831 | 0,498233 | TPU | black | 2,7 |
| mobilephones | MP_O_15 | mobile phone old | LG | KG320S | 2006 | 0,978343 | 0,152365 | 15,573761 | 0,758896 | ASA | silver | 1,7 |
| mobilephones | MP_O_16 | mobile phone old | Sony Ericsson | K750i | 2006 | 0,732114 | 0,040438 | 5,523479 | 0,873615 | n/a | black | 0,7 |
| mobilephones | MP_O_17 | mobile phone old | Sony Ericsson | K800i | 2006 | 2,362221 | 0,186885 | 7,91142 | 1,711464 | n/a | black | 1,2 |
| mobilephones | MP_O_18 | mobile phone old | Sony Ericsson | W580i | 2007 | 1,487784 | 0,117709 | 7,911666 | 0,729068 | ASA | beige/mc | 1,8 |
| mobilephones | MP_O_19 | mobile phone old | Samsung | B2100 | 2009 | 1,181013 | 0,044669 | 3,7823 | 0,691868 | PUR | black | 1,3 |
| mobilephones | MP_O_20 | mobile phone old | Samsung | GT-B2710 | 2010 | 1,047706 | 0,029698 | 2,834549 | 0,776377 | PMMA | silver | 1,3 |

*Flat screen back sides complete table*

| category | Sample | subcategory | brand | model | year | Mean pH ka | std ph ka | cv% ph ka | ka/kb ratio | plastic type | color | thickness (mm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| flatscreen | FS_BS01 | backside | Acer | AL712 | 2003 | 1,257693 | 0,059168 | 4,704453 | 0,567897 | ABS+PC | beige | 2,7 |
| flatscreen | FS_BS02 | backside | Benq | T705 | 2008 | 548,589864 | 2,817973 | 0,513676 | 6,990558 | ABS | black | 2,2 |
| flatscreen | FS_BS03 | backside | HP | LI700 | 2003 | 1425,505778 | 4,800255 | 0,33674 | 6,792889 | PS | black | 2,4 |
| flatscreen | FS_BS04 | backside | Samsung | 943BM | 2008 | 1420,582764 | 14,588424 | 1,026932 | 6,855852 | ABS+HIPS | black | 2,5 |
| flatscreen | FS_BS05 | backside | Samsung | B2240BM | 2011 | 65,176023 | 1,271274 | 1,950525 | 6,013119 | HIPS+ABS | black | 2,7 |
| flatscreen | FS_BS07 | backside | Samsung | 226BW | 2007 | 1,536242 | 0,091284 | 5,942053 | 0,684529 | ABS+HIPS | black | 2,3 |
| flatscreen | FS_BS09 | backside | Samsung | 524B420BW | 2013 | 41,961756 | 0,738124 | 1,759041 | 5,807212 | HIPS+ABS | black | 2,4 |
| flatscreen | FS_BS10 | backside | Asus | VS228 | 2015 | 61,906743 | 0,58102 | 0,938541 | 6,033861 | ABS | black | 2,1 |
| flatscreen | FS_BS11 | backside | Asus | VK222 | 2009 | 1,31206 | 0,036099 | 2,751294 | 0,618851 | ABS+SAN | black | 2,2 |
| flatscreen | FS_BS13 | backside | Dell | 1702FP | 2008 | 1,383595 | 0,072543 | 5,243096 | 0,61314 | ABS+PC | black | 1,8 |
| flatscreen | FS_BS14 | backside | Fujitsu Siemens | C17-2 | 2005 | 1,399105 | 0,036059 | 2,57728 | 0,707574 | n/a | grey | 2,5 |
| flatscreen | FS_BS15 | backside | HP | D5064 | 2002 | 51,770783 | 1,1102 | 2,144453 | 5,732084 | ABS+SAN | black | 3,3 |
| flatscreen | FS_BS16 | backside | Samsung | 1515 | 2002 | 1,572518 | 0,214204 | 13,621695 | 0,567106 | ABS | black | 2,9 |
| flatscreen | FS_BS17 | backside | Acer | AL506 | 2005 | 1,295102 | 0,174074 | 13,440969 | 0,646532 | ABS | beige | 2,6 |
| flatscreen | FS_BS18 | backside | HP | 20555SH249 | 2007 | 4,429787 | 0,265505 | 5,993636 | 2,655218 | ABS | black | 1,6 |
| flatscreen | FS_BS19 | backside | Media | MD5042OC | 2002 | 8,994504 | 0,194436 | 2,161716 | 3,700359 | ABS+HIPS | grey | 2,1 |
| flatscreen | FS_BS20 | backside | HP | P9621D | 2015 | 123,877569 | 0,528227 | 0,426411 | 6,602452 | ABS+SAN | black | 2,6 |
| flatscreen | FS_BS21 | backside | Benq | Q9T5 | 2007 | 5,503724 | 0,225693 | 4,100733 | 2,559291 | ASA+ABS | black | 2,1 |
| flatscreen | FS_BS22 | backside | Iiyama | ProLite 38a | 2002 | 1,510048 | 0,057683 | 3,819945 | 0,756118 | PPE+HIPS | beige | 2,6 |
| flatscreen | FS_BS23 | backside | Philips | 190P6 | 2006 | 14,613409 | 0,262946 | 1,799347 | 3,820003 | n/a | grey | 3,2 |
| flatscreen | FS_BS24 | backside | Meditec | SHB-1756 | 2006 | 1,438242 | 0,071358 | 4,961439 | 0,624399 | ASA+ABS | beige | 2,6 |
| flatscreen | FS_BS25 | backside | Acer | AL1721 | 2003 | 2,032226 | 0,105385 | 5,185688 | 0,871782 | ABS | beige | 2,8 |
| flatscreen | FS_BS26 | backside | Benq | FP93G | 2007 | 12,736474 | 0,88392 | 6,940065 | 4,071195 | ABS+SAN | black | 2,2 |
| flatscreen | FS_BS27 | backside | Samsung | 713BM5 | 2005 | 1,481129 | 0,084237 | 5,687368 | 0,508147 | ABS | black | 2,5 |
| flatscreen | FS_BS28 | backside | HP | 20555 | 2007 | 11,130528 | 0,596509 | 5,359216 | 4,419651 | ABS+SAN | black | 1,6 |
| flatscreen | FS_BS29 | backside | Gericom | 51702D | n/a | 1,737945 | 0,150387 | 8,653171 | 0,667003 | ABS | black | 3,1 |
| flatscreen | FS_BS6 | backside | Belinea | 1730S1 | n/a | 112,673408 | 0,829978 | 0,736622 | 6,42623 | ABS | black | 2,6 |

*Flat screen front sides complete table*

| category | Sample | subcategory | brand | model | year | Mean pH ka | std ph ka | cv% ph ka | ka/kb ratio | plastic type | color | thickness (mm) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| flatscreen | FS_FS01 | frontside | Acer | AL712 | 2003 | 1,467256 | 0,051509 | 3,510558 | 0,654437 | ABS+PC | beige | 2,6 |
| flatscreen | FS_FS02 | frontside | Benq | T705 | 2008 | 10,629824 | 0,286865 | 2,698683 | 4,310226 | ABS | silver | 1,4 |
| flatscreen | FS_FS03 | frontside | HP | LI700 | 2003 | 1,952085 | 0,016363 | 0,838249 | 0,854327 | PMMA | silver | 2,6 |
| flatscreen | FS_FS04 | frontside | Samsung | 943BM | 2008 | 1,258303 | 0,136905 | 10,880106 | 0,695225 | ABS | silver | 2,1 |
| flatscreen | FS_FS05 | frontside | Samsung | B2240BM | 2011 | 1,520448 | 0,028055 | 1,845212 | 0,661682 | ABS | black | 2,5 |
| flatscreen | FS_FS06 | frontside | Belinea | 1730S1 | n/a | 192,515991 | 2,738292 | 1,422371 | 6,930325 | PMMA | silver | 2,1 |
| flatscreen | FS_FS07 | frontside | Samsung | 226BW | 2007 | 1,859615 | 0,074287 | 3,994742 | 0,726736 | ABS | black | 2,6 |
| flatscreen | FS_FS09 | frontside | Samsung | 524B420BW | 2013 | 1,221045 | 0,020502 | 1,679067 | 0,613379 | ABS+SAN | black | 2 |
| flatscreen | FS_FS10 | frontside | Asus | VS228 | 2015 | 94,00897 | 2,00085 | 2,128361 | 6,153597 | ABS HIPS | black | 2,6 |
| flatscreen | FS_FS11 | frontside | Asus | VK222 | 2009 | 1,569615 | 0,044687 | 2,847009 | 0,712701 | ASA | black | 2,6 |
| flatscreen | FS_FS13 | frontside | Dell | 1702FP | 2008 | 1,462554 | 0,074311 | 5,080925 | 0,636348 | PC+ABS | grey | 3 |
| flatscreen | FS_FS14 | frontside | Fujitsu Siemens | C17-2 | 2005 | 1,336646 | 0,037722 | 2,82216 | 0,681861 | PC+ABS | silver | 2,1 |
| flatscreen | FS_FS15 | frontside | HP | D5064 | 2002 | 51,747555 | 0,20667 | 0,399382 | 5,534406 | ASA+SAN+ABS | beige | 3,3 |
| flatscreen | FS_FS16 | frontside | Samsung | 1515 | 2002 | 1,531244 | 0,093931 | 6,134273 | 0,635368 | ABS | silver | 3,1 |
| flatscreen | FS_FS17 | frontside | Acer | AL506 | 2005 | 1,30151 | 0,211862 | 16,27819 | 0,725338 | ABS+ASA | beige | 2,2 |
| flatscreen | FS_FS18 | frontside | HP | 20555SH249 | 2007 | 1,180327 | 0,012927 | 1,095221 | 0,674006 | ABS+PC | silver | 2,4 |
| flatscreen | FS_FS19 | frontside | Media | MD5042OC | 2002 | 1,604175 | 0,047862 | 2,983596 | 0,646599 | PMMA+ABS | silver | 3,1 |
| flatscreen | FS_FS20 | frontside | Benq | Q9T5 | 2007 | 1,390771 | 0,09831 | 7,068724 | 0,635403 | ABS | beige | 2,7 |
| flatscreen | FS_FS21 | frontside | HP | P9621D | 2015 | 1,519725 | 0,098027 | 6,450284 | 0,616334 | PMMA+ABS | silver | 2,6 |
| flatscreen | FS_FS22 | frontside | Iiyama | ProLite 38a | 2002 | 25,856309 | 1,020971 | 3,948633 | 4,73669 | HIPS | beige | 3,2 |
| flatscreen | FS_FS23 | frontside | Philips | 190P6 | 2006 | 739,746806 | 15,307397 | 2,069275 | 6,715398 | PC+ABS | silver | 2,4 |
| flatscreen | FS_FS24 | frontside | Meditec | SHB-1756 | 2006 | 1,669499 | 0,058973 | 3,532356 | 0,575342 | PMMA | black | 3,1 |
| flatscreen | FS_FS25 | frontside | Acer | AL1721 | 2003 | 2,299464 | 0,046594 | 2,026294 | 0,99982 | ABS+SAN | grey | 2,7 |
| flatscreen | FS_FS26 | frontside | Benq | FP93G | 2007 | 1,635768 | 0,041436 | 2,533123 | 0,670011 | PE+PC+ABS | silver | 2,8 |
| flatscreen | FS_FS27 | frontside | Samsung | 713BM5 | 2005 | 3092,837728 | 43,487376 | 1,406067 | 6,13496 | PMMA+ABS | silver | 2,8 |
| flatscreen | FS_FS28 | frontside | HP | 20555 | 2007 | 1,195534 | 0,049704 | 4,157446 | 0,625306 | ABS | silver | 1,7 |
| flatscreen | FS_FS29 | frontside | Gericom | 51702D | n/a | 1,789337 | 0,197847 | 11,057028 | 0,683921 | PE+PC+ABS | silver | 3,1 |

*Large equipment complete table*

| category | Sample | subcategory | brand | model | Mean pH ka | std ph ka | cv% ph ka | ka/kb ratio | plastic type | color | thickness (mm) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| large equipment | LE_01 | WM | Indesit | IWE8168 | 0,998251 | 0,039966 | 4,003632 | 0,833071 | ABS | white | 1,6 |
| large equipment | LE_02 | WM | Bauknecht | IK Care 6B | 0,992134 | 0,090761 | 9,148061 | 0,704871 | ASA+ABS | white | 1,3 |
| large equipment | LE_03 | DW | AEG | n/a | 1,384597 | 0,046049 | 3,325825 | 0,618912 | ABS | black | 2,5 |
| large equipment | LE_04 | WM | Privileg | Basic 76 | 1,133109 | 0,015376 | 1,357005 | 0,694434 | ABS | white | 2,3 |
| large equipment | LE_05 | DW | Miele | G647 | 1,34569 | 0,224575 | 16,688438 | 0,767731 | ABS | white | 2,1 |
| large equipment | LE_06 | DW | Miele | G676 | 1,280441 | 0,054263 | 4,237826 | 0,719114 | ABS | white | 2,6 |
| large equipment | LE_07 | DW | Zanussi | ZDTS 101 | 1,349616 | 0,083465 | 6,184374 | 0,670309 | ABS+SAN | silver | 2,4 |
| large equipment | LE_08 | WM | Whirlpool | n/a | 1,172039 | 0,018758 | 1,600467 | 0,67895 | ABS+SAN | white | 3,1 |
| large equipment | LE_09 | DW | AEG | GS60AIB | 0,992201 | 0,120452 | 12,139922 | 0,644085 | n/a | black | 1,5 |
| large equipment | LE_10 | WM | Siemens | Wash & Dry 1220 | 0,912729 | 0,082202 | 9,006227 | 0,697909 | ABS | white | 1,3 |

*Kitchen equipment complete table*

| category | Sample | subcategory | brand | Mean pH ka | std ph ka | cv% ph ka | ka/kb ratio | plastic type | color | thickness (mm) |
|---|---|---|---|---|---|---|---|---|---|---|
| kitchen equipment | KE_01 | WK | Siemens | 0,773441 | 0,092439 | 11,951596 | 0,78075 | ?? | white | 1,1 |
| kitchen equipment | KE_02 | WK | TCM | 1,274273 | 0,144945 | 11,374715 | 0,602013 | PP | white | 2,4 |
| kitchen equipment | KE_03 | WK | SimPexBasic | 1,414105 | 0,0651 | 4,603623 | 0,675031 | PP | black | 2,3 |
| kitchen equipment | KE_04 | SMX | Moulinex | 1,274834 | 0,037672 | 2,955081 | 0,583771 | ABS | white | 2,6 |
| kitchen equipment | KE_05A | MX | Moulinex | 19,090321 | 0,204142 | 1,069347 | 5,179626 | ABS | white | 1,8 |
| kitchen equipment | KE_05B | MX | Moulinex | 397,965281 | 6,687115 | 1,680326 | 6,69263 | ABS | black | 2 |
| kitchen equipment | KE_06 | MX | Ciatronic | 1,623897 | 0,07856 | 4,837734 | 0,531106 | ABS+ASA | white | 2,3 |
| kitchen equipment | KE_08 | T | Kenwood | 1,266325 | 0,1467 | 11,584724 | 0,733245 | PP | white | 2,1 |
| kitchen equipment | KE_09 | T | Severin EG | 1,194553 | 0,035125 | 2,940463 | 0,598935 | PP | white | 2,4 |
| kitchen equipment | KE_10A | T | Lutter+Parter Studio | 1,241317 | 0,052213 | 4,206294 | 0,648406 | PP | white | 2,7 |
| kitchen equipment | KE_10B | T | Lutter+Parter Studio | 1,201885 | 0,0812 | 6,756095 | 0,636774 | PP | grey | 2,4 |
| kitchen equipment | KE_11 | T | Russell Hobbs | 1,608717 | 0,138832 | 8,630007 | 0,691467 | PP | black | 3 |
| kitchen equipment | KE_12 | T | Bosch | 1,364807 | 0,056119 | 4,111887 | 0,677377 | PP | black | 2,3 |
| kitchen equipment | KE_13 | T | TCM | 1,265147 | 0,058609 | 4,632595 | 0,652281 | PP | blue | 2,6 |
| kitchen equipment | KE_14A | KM | Bosch | 1,271352 | 0,060131 | 4,729693 | 0,526072 | ABS | white | 2,3 |
| kitchen equipment | KE_15 | WK | Severin EG | 1,38721 | 0,125432 | 9,04205 | 0,643012 | PP | white | 2,5 |
| kitchen equipment | KE_16 | MX | Trion | 1,385877 | 0,127249 | 9,181841 | 0,675409 | ABS | white | 2,4 |
| kitchen equipment | KE_17 | T | Maltatech | 32,149163 | 0,197427 | 0,614098 | 4,175688 | PP | black | 2,3 |
| kitchen equipment | KE_18 | WK | Severin EG | 1,178026 | 0,114588 | 9,727139 | 0,712715 | PP | white | 1,8 |
| kitchen equipment | KE_19 | SMX | Moulinex | 1,359348 | 0,014733 | 1,083838 | 0,74163 | ABS | white | 2,6 |
| kitchen equipment | KE_20 | SMX | ESGE | 1,30291 | 0,069515 | 5,335362 | 0,661392 | ABS | white | 2,2 |
| kitchen equipment | KE_22 | KM | Superespresso | 1,34755 | 0,048855 | 3,625443 | 0,391849 | ABS | grey | 2,3 |
| kitchen equipment | KE_23 | KM | Nespresso | 1,633768 | 0,151489 | 9,272392 | 0,688945 | ABS | black | 2,5 |
| kitchen equipment | KE_24 | ES | AEG | 1,186621 | 0,05205 | 4,386389 | 0,730522 | ABS | n/a | 2,5 |
| kitchen equipment | KE_25 | CU | Kenwood | 1,422118 | 0,113495 | 7,980729 | 0,561325 | ABS | n/a | 3 |
| kitchen equipment | KE_27B | WK | TCM | 1,211332 | 0,041035 | 3,387556 | 0,597786 | PP | white | 2,4 |
| kitchen equipment | KE_28 | KM | Nespresso | 1,778403 | 0,113093 | 6,359252 | 0,666716 | ABS | red | 3,1 |
| kitchen equipment | KE_29 | KM | Nespresso | 1,372934 | 0,075765 | 5,518474 | 0,59052 | ABS | black | 2,6 |
| kitchen equipment | KE_30 | KM | Nespresso | 1,485315 | 0,093367 | 6,286013 | 0,617644 | ABS+PC | black | 2,6 |