

BFRs in Electric and Electronic Equipment Waste

EU regulations and solvothermal extraction to benefit plastic recycling

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<p>Abstract:</p> <p>This thesis is describing the modern situation of brominated flame retardants in the European union today. Directives of many kinds are made for all sorts of purposes concerning brominated flame retardants. Brominated flame retardants are highly bio-accumulative, and therefore directives are there to protect the nature and human from hazardous substances. The main directives concerning brominated flame retardants are REACH – Regulation, Waste of Electric and Electronic Equipment Directive, Restrictions of Hazardous Substances Directive, Water framework Directive and marketing concerning directives. RoHS – Directive is evaluating chemicals placed on the market in the European Union and has set a limitation of 1w% for brominated flame retardants in plastics. The three main brominated flame retardants used nowadays are tetrabromobisphenol A, polybrominated diphenyl ether and hexabromocyclododecane. Of these the most used tetrabromobisphenol A, followed by polybrominated diphenyl ether and hexabromocyclododecane. tetrabromobisphenol A is mostly used because of REACH – Regulation declared tetrabromobisphenol A safe for human health and environment when used less than 1% of the weight in a homogeneous polymer matrix. Brominated flame retardants are not recyclable with other plastic waste. Therefore, the need for picking out and sorting of plastics containing BFRs. The plastic itself is recyclable if the polymer is free from bromine, which leads to the need of finding ways of separating bromine from the polymer matrix. Among other, different extraction methods are used for this purpose and consequently the extraction is a part of this thesis. Solvothermal extraction was performed and samples analyzed with FTIR and UV-Vis-NIR.</p>	
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<p>Sammandrag:</p> <p>I detta examensarbete behandlas situationen om brominerade flamskyddsmedel inom Europa idag. Brominerade flamskyddsmedel är mycket bioackumulerande och därför finns det direktiv för att skydda människan och naturen från hälsoskadliga ämnen. Direktiv av många slag finns gjorda för olika typer av ändamål, de viktigaste direktiven gällande brominerade flamskyddsmedel är REACH – förordningen, WEEE – Direktivet, RoHS – Direktivet, Vattendirektivet och direktiv gällande marknadsföring. RoHS – direktivet utvärderar kemikalier som släpps kommer in eller släpps ut på marknaden inom Europeiska unionen, och har satt en begränsning på att brominerade flamskyddsmedel inte får överskrida 1% av den totala viken av plastföremålet. De tre viktigaste och mest använda brominerade flamskyddsmedlen inom Europeiska unionen idag är tetrabromobisphenol A, Polybrominerade difenyletrar och Hexabromocyclododecane. Av dessa används tetrabromobisphenol A helt klart mest, främst på grund av att ämnet blivit deklarerat säkert för människor när ämnet används inom givna gränser av REACH – förordningen. Brominerade flamskyddsmedel är inte återvinningsbara med annat plastavfall, därav behovet att kunna sortera bort plaster innehållande brom vid avfallsstationer. Plasten i sej själv kan återvinnas så länge polymeren är fri från brom. Därutav kommer behovet att kunna separera bromet från polymer kedjan. Bland annat används olika extraktionsmetoder för detta ändamål och därmed utgör extraktion en del av examensarbetet. Lösningsextraktion i ugn utfördes och extrakten analyserades med en FTIR och UV-Vis-NIR.</p>	
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Abbreviations

ABS	Acrylonitrile butadiene styrene
BFR	brominated flame retardant
BSEF	Bromine Science and Environmental Forum
CLH	Harmonized classification of labelling
E&E	electrical and electronic
ECHA	European Chemical Agency
EEA	European Environment Agency
EEE	electrical and electronic equipment
EFRA	European Flame Retardants Association
EPS	Expanded polystyrene
EU	European Union
FTIR	Fourier Transform Infrared Spectrometer
HBCD	hexabromocyclododecane
HIPS	High-impact polystyrene
PBB	polybrominated biphenyl
PBDE	polybrominated diphenyl ether
PBT	Polybutylene terephthalate
PCB	Printed circuit board
PFOS	Perfluorooctanesulfonic acid
POP	Persistent Organic Pollutants
PP	Polypropylene
PUR	Polyurethane
REACH	Registration, Evaluation, Authorization and Restriction of Chemicals
RoHS	Restriction of use of certain Hazardous Substances
RoI	Registry of Intentions
SVHC	Substances of Very High Concern
SVT	Suomen virallinen tilasto (Official Statistics of Finland)
TBBPA	tetrabromobisphenol A
UV-Vis-NIR	Ultraviolet Visible Near-infrared
VECAP	The Voluntary Emissions Control Action Programme
WEEE	electric and electronic waste

WFD Water Framework Directive

XPS Extruded polystyrene

1 INTRODUCTION

1.1 Background

The identification and recycling of plastics containing hazardous flame retardants is a problem of very high concern. The strive for recycling of materials are high and more is demanded each year. Complications with plastics containing hazardous substances are that they are not allowed among the ordinary “clean” waste, that proceed for recycling. The restrictions and limits for harmful substances in plastics are existing, but the world is still containing old products, where materials are exceeding the limits.

There is a need for methods in removal of the hazardous ingredients so that they will not end up in landfill and continue degrading in the nature. The complete removal of Brominated Flame Retardants, BFRs, from the polymeric chain is preferable and would lead to the plastic itself being recyclable with other clean plastic waste.

1.2 Objectives

The objectives in this study is to summarize and gather information about the situation of brominated flame retardants today, with a focus on restrictions in the EU. Also, an experimental attempt for this thesis is to try out and re-make an extraction of brominated flame retardants from plastic waste. The extraction is based on a study made by Zhang & Zhang, 2014, “Removal of brominated flame retardant from electrical and electronic waste plastic by solvothermal technique”. The objectives will therefore be; (1) bring a fresh knowledge about the restrictions and directives active in EU today, (2) is the solvothermal process working, and (3) is it possible to analyze the extracts with UV-Vis-NIR.

2 LITERATURE REVIEW

2.1 Brominated flame retardants

European Flame Retardants Association (EFRA) inform that flame retardants are used as additives in plastics for improving fire safety in the surrounding environment. Flame retardants have high melting temperatures and increase the time of starting a fire. They reduce the spreading of a fire and the amount of heat dissipated to save lives. The total amount of toxic gases (e.g. Carbon monoxide) are cut down with a third when flame retardants are present. (EFRA - European Flame Retardants Association, 2007) Every plastic, rubber and textiles are containing flame retardants.

This project is going to focus on Brominated Flame Retardants. BFRs are typically used in electronics, vehicle parts of plastic and interiors because of the excellent flame retardant properties. It is necessary to add flame retardants to reach up to the safety standards and directives set for electronics nowadays. The main requirements the product needs to stand up for are general safety regulations, product standards and fire test standards. (EFRA - European Flame Retardants Association, 2007)

Table 1. Safety standard for plastic products (EFRA - European Flame Retardants Association, 2007)

Requirements	Examples	
General safety regulations	EU General Product Safety Directive 2001/95/EC	Construction Products Directive 89/106/EC
Product standards	IEC 60065 for television sets and other audio/video	EN 13162 ... 13171 for thermal insulation products for buildings
Fire test standard	UL 94 flammability standard	Single Burning Item Test, EN 13823

Bromine Science and Environmental Forum (BSEF) is an organization that represents the whole bromine industry to inform decision-makers and research projects about brominated flame retardants that involve human health. Flame retardants containing bro-

mine are highly accumulating in living organisms and therefore the interest in the study of BFRs. (Bromine Science and Environmental Forum, u.d.)

According to BSEF, the three main groups of BFRs are Deca-diphenyl ether (Deca-BDE), tetrabromobisphenol A (TBBPA) and hexabromocyclododecane (HBCD). The most used BFR is TBBPA followed by polybrominated diphenyl ethers (PBDE) and HBCD. PBDE has a total amount of 209 isomers, where some occur in manufactured mixtures with Penta-BDE, Octa-BDE and Deca-BDE. Deca-BDE is the most used of the PBDE isomers, as mentioned earlier. (BSEF, 2012)

The Voluntary Emissions Control Action Programme (VECAP) is run by BSEF, a program under Responsible Care Initiative, to set standards for chemical management along the value chain from manufacturing to waste. It is a voluntary emission of member countries of the EFRA, European Flame Retardant Association. The initiative began with textile industry in UK and as the program was adapted wider, it concerns now BFRs in the European textile and plastic industry. (Bromine Science and Environmental Forum, u.d.)

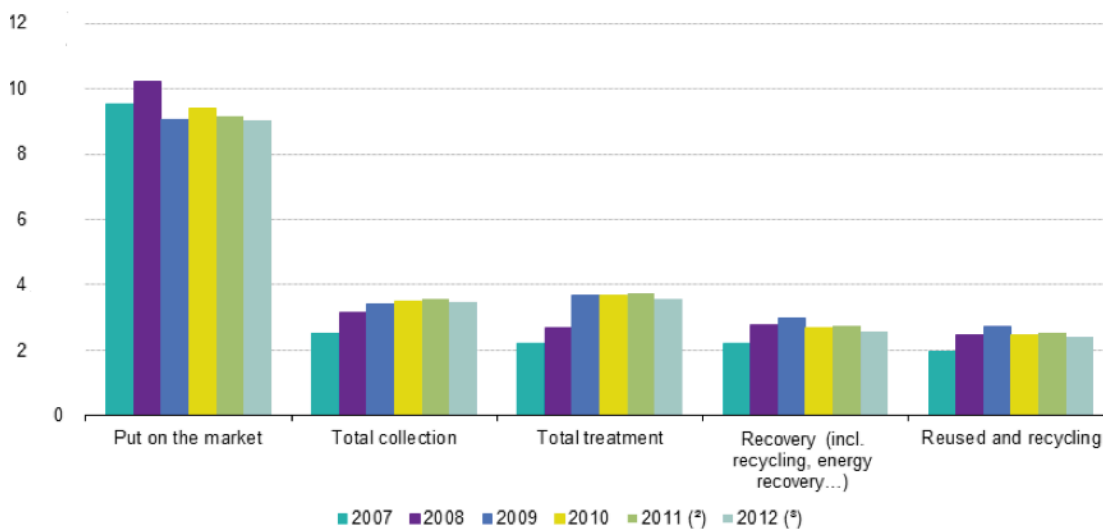
European Environment Agency (EEA) provides information for decision-makers in developing, adopting, implementing and evaluating environmental strategies. EEA regulations were adopted by EU in 1990 and has today 33 member countries. The regulation is helping members making decisions in improving and boosting the environmental and economic benefits of recycling. (European Environment Agency (EEA), 2015)

Today recycling Waste of Electric and Electronic Equipment (WEEE) containing BFRs are delivering satisfactory results, compared to other flame retardants. Most commonly used brominated flame retardants, as TBBPA, are fully compatible with modern waste management systems. Studies of EU Risk Assessment reports show that EU regulations for WEEE waste is sustained and that it is possible to handle the electronic appliances in an environmentally friendly and trustworthy way. However, recycling of plastics containing BFRs is not always possible due to relatively small amounts of BFR containing waste among the large volume of plastic waste rolling in. (Bromine Science and Environmental Forum, u.d.)

2.1.1 Waste of Electric and Electronic Equipment

TV-housings and computer monitors are used for the experiment, therefore information about electronic waste is further focused on. According to European Commission, Waste of Electric and Electronic Equipment, WEEE, is a category that consists of; computers, TV-sets, fridges and cell phones. Electronic waste is one of the most rapidly expanding fields of waste nowadays in the EU, with 9 million metric tons placed on the market 2005, when the European Commission laid down the directive on rules for WEEE waste. (European Commission, 2015)

As seen in the Figure 1 from Eurostat, the statistical office of the European Union, 2007 – 2012 still lays around 9 million metric tons placed on the market in Europe. From 2007 there can be seen an increase of gathered and recycled WEEE to 2009, but from there on, no big changes have occurred. As seen in figure 1, most of the gathered WEEE are reused and recycled.



(*) Includes Eurostat estimates due to missing data for several EU Member States.

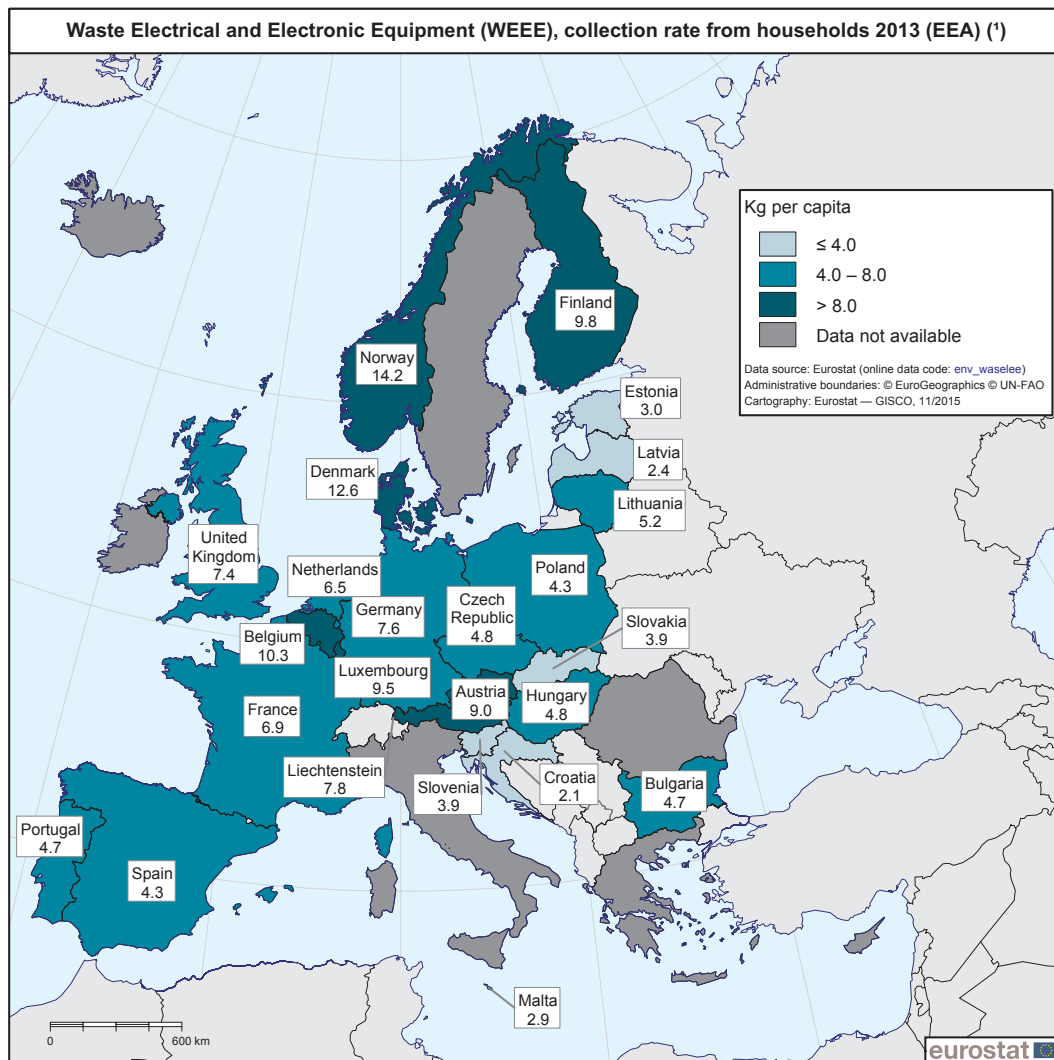
(*) Does not include data for Croatia on reuse and recovery.

(*) Includes data for EU-28.

Figure 1. 2007 - 2012, Electrical and electronic equipment (EEE) put on the market and collected as waste (WEEE). Values in million metric tons on y-axis. (Eurostat, 2015)

From today until 2019, the WEEE Directive - Directive 2012/19/EU, has a target of reaching a minimum of 4 kg per year per inhabitant gathered of WEEE waste. From 2018 the directive will extend from current restrictions to all categories of EEE.

(Eurostat, 2015) More about the WEEE Directive upcoming. A picture is added down below, figure 2, for demonstrating that most of EU countries are doing fairly well when it comes to gathering of waste of electric and electronic equipment.



(*) European Economic Area: [http://ec.europa.eu/eurostat/statistics-explained/index.php/Glossary:EEA_\(1\)](http://ec.europa.eu/eurostat/statistics-explained/index.php/Glossary:EEA_(1))

Figure 2 Collected amounts of WEEE waste from households in each country and per inhabitant. (Eurostat, 2015)

A recent study was made in Finland about amount of general waste expected to year 2030. Evidently, the amount of waste is and will be increasing. Total amount of waste gathered in Finland 2013 was 96 061 137 metric tons, whereas 1 702 184 metric tons was marked as hazardous waste. Among the hazardous waste, rubber lays at 16 024 metric tons and plastics 64 934 metric tons. Printed circuit boards have a column of its own, and 983 metric tons hazardous printed circuit board waste was gathered. (Suomen virallinen tilasto (SVT), 2013) The amount of total waste ending up in landfill in Fin-

land 2012 was 48 015 000 metric tons, which gives about 53% of the total collected waste in 2012. (Eurostat, 2015)

The municipal waste is standing for 59% of the total waste. Municipal waste refers to waste gathered from peoples' garbage cans at home and in public places. The other 41 % is public activities, stores and private services waste. As viewed in Figure 3, the total amount of mixed waste gathered from the community in 2014 was 2 600 000 metric tons. 1 300 000 metric tons was brought to energy recovery, burnable waste. 460 000 tons was delivered to landfill and remaining 856 000 metric tons was recycled or reused as new material. (Suomen virallinen tilasto (SVT), 2013)

Municipal waste by treatment method in 2002 to 2014

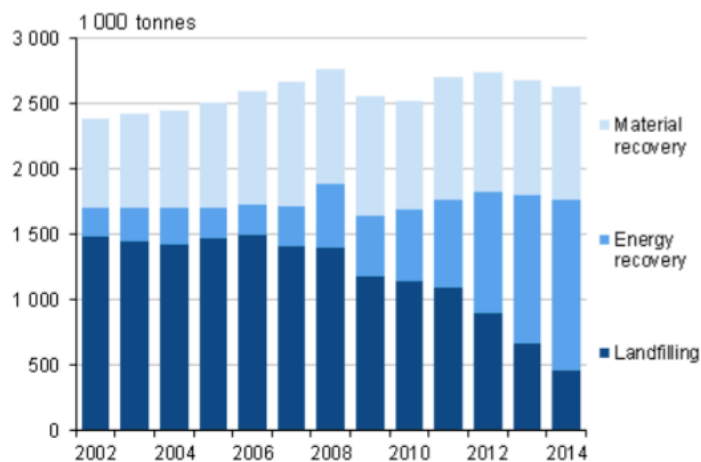


Figure 3. Municipal waste in Finland 2002 - 2014. (Suomen virallinen tilasto (SVT), 2013)

Under the category for electronic waste, 59 373 metric tons was gathered, 59 333 metric tons was recycled and 40 metric tons sent for energy use, leaving nothing to end up in landfill. Electronic waste is a mixture of many materials and components, which can cause great danger for the environment and human health by the additive mixtures when dissipated from the materials. Several EU directives are made for electronic waste, the directive on Electrical and Electronic Equipment (WEEE Directive) mentioned before, is handling collection schemes for consumers to return WEEE waste free of charge from 2002. The directive was renewed 2012 and adding the information for handling of the waste stream.

Another is the directive on the Restriction of the use of Certain Hazardous Substances in Electrical and Electronic Equipment (RoHS Directive) from 2003. The directive handles heavy metals and flame retardants as PBBs and PBDEs to be replaced with safer substitutes. More about the different directives upcoming. (European Commission, 2015)

2.1.2 Persistent Organic Pollutants

Persistent Organic Pollutants, POPs, are carbon-based organic substances that persist and accumulate in the environment and risk danger the human health through the food chain. They tend to bioaccumulate in human and animal fat tissue and are capable of long-range transport that eventually will end up in causing serious health problems. The combination of physical and chemical properties makes them stay intact for very long periods and spread with living organisms, water, soil and air.

The Stockholm Convention took an effect in May 2004 on Persistent Organic Pollutants, and today POPs are regulated by the EU Regulation (EC) No 850/2008. The convention is globally active to protect the human health and environment from hazardous chemicals. The convention lists pollutants that are unsafe, prohibits and/or eliminates production of internationally produced POPs. (Secretariat of the Stockholm Convention, 2016) An update of the regulation came into force in June 2015, which creates minimum concentration limits for polybrominated diphenyl ethers (PBDE) and perfluorooctane sulfonic acid (PFOS). Also, the new regulation adds a few substances to the “list of controlled by regulation”, along with POPs listed by the Stockholm Conventions and Long-Range Trans boundary Air Pollutants. (Essenscia, 2014)

The convention arranges chemicals into Annex A, Annex B and Annex C, where Annex A is meaning to prohibit and/or eliminate the production of the pollutant. Annex B is restricting the production and use for acceptable conditions and C is the category for unintentional production, to minimize and finally eliminate the substance in question. Below in table 2 is listed chemicals targeted by Stockholm Convention and registered as POPs. In the list can be found in Annex A four BFRs which are highlighted. Dioxins and furans put under Annex C are unintentional byproducts of incomplete combustion in the manufacture process of pesticides, chlorinated substances and also a possible by-

product of re-heating and processing of plastics containing BFRs. (Secretariat of the Stockholm Convention, 2016)

Table 2. Stockholm Convention listed POPs. (Secretariat of the Stockholm Convention, 2016)

Annex A (Elimination)	Aldrin	Chlordane	Chlordecone
	Dieldrin	Endrin	Heptachlor
	Hexabromobiphenyl	Hexabromocyclododecane (HBCD)	Hexa- and hepta-bromodiphenyl ether (components for Octa-BDE)
	Hexachlorobenzene (HCB)	Alpha hexachloro-cyclohexane	Beta hexachloro-cyclohexane
	Lindane	Mirex	Pentachlorobenzene
	Polychlorinated biphenyls (PCB)	Technical endosulfan and its related isomers	Tetra- and pentabromodiphenyl ether (PBDE)
	Toxaphane		
Annex B (restriction)	Dichlorodiphenyl-trichloroethane (DDT)	Perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride	
Annex C (Unintentional production)	Hexachlorobenzene (HCB)	Pentachlorobenzene	Polychlorinated biphenyls (PCB)
	Polychlorinated dibenzo- <i>p</i> -dioxins (PCDD)	Polychlorinated dibenzofurans (PCDF)	

2.1.3 REACH Regulation

In 2006 an EU regulation came into the picture when it comes to outlining Registration, Evaluation, Authorization and Restriction of Chemicals, REACH. REACH aims to, as

the other conventions, protect human health and environment while allowing and taking into account the proficiency of the EU chemicals industry. The REACH regulation (Regulation EC No 1907/2006) keeps a register on produced chemicals and substances imported to the European Authorities. In order to register a product, a report must be submitted to the European Chemical Agency – ECHA. (Bromine Science and Environmental Forum, u.d.) ECHA is the main regulatory authorities in applying EU's chemical legislation for protecting the human health, environment, innovation and competition. ECHA is providing information for companies to use safe chemicals. (ECHA - European Chemicals Agency, 2015)

In 2012 Deca-BDE is submitted to be listed in the Registry of Intentions – RoI, where member states prepare reports for identification of Substances of Very High Concern (SVHC), restrictions and labelling; Harmonized Classification of Labelling. Through the public register existing records can be checked for filed chemical substances, so that no double work needs to be done. TBBPA and HBCD were added to the list in 2010. TBBPA is already through with the REACH registration procedure and was concluded to cause no risks or health problems for human or the environment. Hence, there is nothing going on under REACH with TBBPA. The use of HBCD is from August 2015 on, restricted to “only approved uses” in Europe. (Bromine Science and Environmental Forum, u.d.)

2.1.4 WEEE – Directive

Waste Electrical and Electronic Equipment (WEEE), since February 2003, aims to reuse and recycle electronic waste instead of letting them end up in landfill. The directive is made up for all stages of the lifecycle of the electric and electronic equipment. All industries in EU countries are encouraged to advise of the removal, separation of certain components and hazardous substances of the end of life products. The separation is including plastic containing BFRs from any collected electrical and electronic equipment (EEE). (Bromine Science and Environmental Forum, u.d.)

In 2012 a new WEEE directive stepped into force and became active 2014. In the new directive (Directive 2012/19/EU), member countries must from 2016 on collect 45% of

the average Electric and Electronic Equipment, EEE, placed on their countries market. The new directive did not make any changes for BFRs in particular but for the waste handling. 2019 the minimum collected amount of EEE has to be 65% a year of the total amount placed on the market, which means countries must gradually improve the collection rate from 2016 – 2019. (Official Journal of the European Union, 2012) The directive also demands a recovery rate of 70 – 80% and re-use of 50 – 75% of the average waste in 2012 – 2015. From 2016 and on, the rate has to be increased to 75 – 85% and 55 – 80% respectively. (Bromine Science and Environmental Forum, u.d.)

2.1.5 RoHS – Directive

The Restriction of the use of certain Hazardous Substances in Electrical and Electronic Equipment, RoHS, prohibits the EU market with EEE that contains more than approved levels of hazardous substances. The original Directive 2002/95/EC – RoHS was published in January 2003, and updated and replaced by 2011/65/EC – RoHS that stepped in July 2011. (European Commission, 2015)

The directive gives limitations for substances that are not allowed in EU in larger amounts than restricted. The substances concerned are among other; cadmium, mercury, lead, hexavalent, chromium, polybrominated biphenyls (PBB) and polybrominated diphenyl ethers (PBDE) in Electrical and Electronic Equipment. The limitations for PBBs and PBDEs are restricted to maximum 0.1% by mass in homogenous materials, which apply to Electrical and Electronic Equipment placed on the market from 1 July 2006 or within certain transition periods. (Tukes, 2012) The usual PBDEs are Penta-, Octa- and Deca-BDE, whereas Penta-BDE and Octa-BDE are completely banned from the market since 2006. (Bromine Science and Environmental Forum, u.d.)

2.1.6 WFD – Directive

Water Framework Directive (WFD), December 2000, is a strategy for protecting and dealing with polluted water. The directive in 2008 had 33 substances on the list of priority and another 12 is added in 2013. The list contains substances that has to be monitored and priorities potentially hazardous substances. Octa-BDE and Deca-BDE is listed

to be supervised while Penta-BDE is on the list for priority hazardous substance that is prohibited to release into the environment. (Bromine Science and Environmental Forum, u.d.)

2.1.7 Summary table of directives

The mentioned directives are summed up in table 3 according to the regulations for brominated flame retardants in Europe. In the table is also included 4th and 24th time Council Directive 76/767/EEC, which is not mentioned above, is a regulation for marketing and restricting. 24th amendment bans all use of Penta-BDE and Octa-BDE, whereas 4th amendment bans all use of textiles containing PBB from the European market. Table is made by Bromine Science and Environmental Forum.

Table 3. Regulations summarized from directives point of view. (Bromine Science and Environmental Forum, u.d.)

Legal basis	Content	Deadline for compliance	BFR substance concerned
WEEE Directive	Separation of BFR plastics from E&E equipment prior to recovery and recycling	December 2006	All BFRs used in E&E
RoHS Directive	Ban of use in E&E applications	1 July 2006	Penta-BDE, Octa-BDE, PBB
	Ban in E&E applications	1 July 2008	Deca-BDE
EU Directive establishing the list of priority substances in the field of water policy	Establishment of controls of emissions, discharges and losses in the environment and water quality standards	Not applicable	Deca-DBE and Octa-BDE
	Cessation of emission in the Environment	2020	Penta-BDE

	Cessation of emissions in the Environment	2033	HBCD
24 th amendment to the marketing and use Directive 76/769/EEC	Ban of use in all applications for the EU market	15 August 2004	Penta-BDE and Octa-BDE
4 th amendment to the marketing and use Directive 76/769/EEC	Ban from textile applications in the EU market	November 1984	PBB (Not produced since 2000)
REACH	Evaluation of all chemical substances placed in the EU market	Registration substances produced or imported with volumes over 1000 tonnes/year and CMR or R50/R53 substances with over 1 tonne/year: 1 December 2010	TBBA, HBCD and Deca-BDE

2.1.8 BFRs of most concern by the directives

Polybrominated diphenyl ethers, PBDEs, is a group consisting of several isomers whereas Deca-BDE, Octa-BDE and Penta-BDE are restricted by the different EU directives. PBDEs have very good flame retardant properties because of the large amount of bromine atoms in the chemical structure, which is why the flame retardant is highly used. (Secretariat of the Stockholm Convention, 2016)

Deca-BDE is present in electrical and electronic equipment as well as in textiles and today registered in REACH since 2010. In 2012 Deca-BDE was proposed and become a substance of very high concern by UK Competent Authorities to ECHA. A Restriction proposal was made for ECHA in August 2014. It is also submitted for listing for the Stockholm Conventions' POPs. The POP Review Committee evaluates the proposals and propose restrictions. (Secretariat of the Stockholm Convention, 2016)

Octa-BDE is mainly used in ABS, HIPS and PBT plastics in form of casings of electronics. Octa-BDE releases substances into the air via emissions of the products, wear and degradation, which is causing de-bromination and ending up in dust particles. The particles are highly accumulating and persistent in the environment. Hence, Octa-BDE is banned of all use in applications for European market since August 2004. (BSEF, 2012)

Penta-BDE is mainly used in polyurethane foam, and released to the air through processing, dismantling and from recycle procedure. The releases into the air and can be found in dust, water, soil and can be inhaled. As for Octa-BDE, Penta-BDE is banned from all use in the EU since 2004. (Secretariat of the Stockholm Convention, 2016)

Polybrominated biphenyls, PBBs, were widely used in plastic products and in textiles. PBB is banned a long time ago and is no longer used nor produced. However, there might still be products of that time when it was widely used. PBBs were mixed into the polymer rather than bonded with the chemical structure of the polymer, which makes the PBB remain in its toxic state and leave the mixture. (Secretariat of the Stockholm Convention, 2016)

Tetrabromodisphenol A, TBBPA, is restricted but not forbidden therefore the most widely used brominated flame retardant. TBBPA usually perform in printed circuit boards which is existing in as good as any electronic device. The additive mixes well with resins used in circuit boards or laminates and becomes a reactive flame retardant, which refers to instead of being a free chemical the molecules attach to the backbone of the polymer resin itself. In May 2005 TBBPA is proven to possess no risk to human health nor the environment. However, TBBPA used in Acrylonitrile Butadiene Styrene, ABS, plastics at a single European plant showed to be a risk. (BSEF, 2012)

TBBPA has been under REACH since October 2010. REACH does not restrict TBBPA itself, but restricts brominated flame retardants in Printed Circuit Boards (PCB) greater than 10 cm². The collected WEEE with PCBs greater than restricted needs separate treatment. Processes of TBBPA are still ongoing under REACH. (BSEF, 2012)

Hexabromocyclodecane, HBCD, is highly toxic to living organisms, especially marine life, and is therefore since 2008 placed in the list of Substances of Very High Concern. HBCD was listed in REACH and today only authorized applications is allowed in EU. Since 2013 HBCD is listed in Annex A in the Stockholm Convention on Persistent Organic Pollutants for elimination with specific criteria for Polystyrene, Expanded- and Extruded Polystyrene (EPS, XPS). After five years, the ban of HBCD together with polystyrene is compulsory. The use and production of HBCD is decreasing and there are already available alternatives on the market. In Table 4 is presented all mentioned BFR substances concerned by the directives and table is made by Bromine Science and Environmental Forum. (Secretariat of the Stockholm Convention, 2016)

Table 4. Summary of the most concerned BFRs and how the risk assessment is completed. (Bromine Science and Environmental Forum, u.d.)

BFR substance	Content	Legal basis	Deadline for compliance	EU scientific risk assessment status
Deca-BDE	Separation of BFR plastics from E&E equipment prior to recovery and recycling	WEEE Directive	December 2006	Finalized in May 2004, now integrated into REACH
	Ban for use in all E&E applications	RoHS Directive	1 July 2008	
	Establish of controls of emissions, discharges and losses in the Environment and water quality standards	EU Directive establishing the list of priority substances in the field of water policy	Not applicable	
Octa-BDE	Separation of BFR plastics from E&E equipment prior to recovery and recycling	WEEE Directive	December 2006	Finalized

	Ban of use in E&E applications	RoHS Directive	July 2006	
	Ban of use in all applications for EU market	24 th amendment to the marketing and use Directive 76/769/EEC	15 August 2004	
	Controls of emissions, discharges and losses in the environment and water quality standards	EU Directive establishing the list of priority substances in the field of water policy	Not applicable	
Penta-BDE	Separation of BFR plastics from E&E equipment prior to recycle	WEEE Directive	December 2006	Finalized
	Ban of use in E&E applications	RoHS Directive	July 2006	
	Cessation of emissions in the environment	EU Directive establishing the list of priority substances in the field of water policy	2020	
	Ban of use in all applications for the EU market	24 th amendment to the marketing and use Directive 76/769/EEC	15 August 2004	
PBB (No longer produced since 2000)	Ban from textile applications in the EU Market	4 th amendment to the marketing and use Directive 76/769/EEC	November 1984	Not applicable

	Ban from E&E applications in the EU Market	RoHS Directive	July 2006	
TBBPA	Separation of BFR plastics from E&E equipment prior to recycling, separation of printed circuit boards	WEEE Directive	December 2006	Finalized. Now integrated into REACH
HBCD	Separation of BFR plastics from E&E equipment prior to recycling	WEEE Directive	14 February 2014	Finalized. Now integrated into REACH
	Cessation of emissions in the environment	EU Directive establishing the list of priority substances in the field of water policy	2033	

2.2 Recycled waste containing BFRs

The directives about WEEE waste claims to re-use and recover as much of the waste as possible. In 2008 the amount of WEEE plastics share in Europe was estimated to 20.6%, which is about 300 000 metric tons of recovered or disposed in a year. (Wäger, et al., 2012) The strive to find new business opportunities and development of plastic recycling techniques is at its top. An urgent need to find new recycling technologies for WEEE before causing any more harm to the environment.

The RoHS Directive for WEEE tells that plastic containing more than 0.1% of brominated flame retardants by weight are not allowed in the same waste line as for recycling of plastic. The detection has to be on line and picked out the plastic notified by hand or by automatic to separate the hazardous from normal waste.

Several plastics containing flame retardants are suitable for mechanical recycling. Flame retardants usually put more economic value to the plastic, hence the recycling is necessary for not losing the economical advantage. Studies show that recycling of ABS containing BFRs are very stable when it comes to reprocessing. The flame retardant properties are kept and the material could be processed four times before it loses its abilities. Same apply to Polypropylene, PP, containing BFRs. PP is recyclable up to eight times for it to maintain fire safety levels, melt flow properties and color. (EFRA - European Flame Retardants Association, 2007)

2.3 Analyzing plastic containing BFRs

2.3.1 Samples

Sample preparation of plastic containing BFRs is generally sample gathering, grinding, extraction, purifying and quantification. BFR plastics are usually directly analyzed onto the solid plastic or then possibly extracted to analyze the extract.

Sample gathering by air is done by active and passive sampling, whereas active sampling is having large volume of air passing through the sample and passive is simply plate exposure. (Xu, et al., 2013) Samples from the environment can also be gathered from dust particles, cloth- and plastic-pieces. The dust may be taken from tables or vacuum cleaners. The samples are placed in a closed bottle, extracted in a liquid and then samples can be analyzed with different methods. The different sampling methods all have in common the gathering on filters or fibers of some sort. The filters are then extracted and analyzed.

Samples directly from people are gathered for example via hand wash with ethanol and the ethanol is then analyzed. From the skin the BFR exposure can be measured with sample patches attached to the skin. The extract will then be analyzed after extraction of the patches.

Extraction is a common method for analyzing solid samples like soil, sediment, absorbent materials from air sampling and biotic samples. Solid plastics are grinded to powder or granolas before the extraction.

After the extraction the wanted extracted substances needs to be cleaned out of the mixture. Halogenated POPs often require a separation into different analytical groups since they tend to coelute, which causes problems with the chromatography making separation and identification hard.

2.3.2 Extraction methods

Extraction of BFRs can be made by many different methods, for example; soxhlet-extraction, ultrasound-extraction, microwave extraction or simply solvent extraction with or without heat. These are a few methods mentioned in several research papers about extraction of BFRs. The usual problem with extractions seems to be that they are time consuming, require sample preparation and many steps before, during and after the extraction.

For this research the extraction method chosen is solvothermal extraction. A research done by Zhang & Zhang, 2014, concerning BFR extraction from electronic waste, was done to evaluate the possibility of a solvothermal process. The procedure was described as follows.

15 ml isopropanol is mixed with 1.0g plastic (liquid to solid ratio 15:1) pellets mixed in a Teflon interior reactor. Reactor is gradually heated to 90°C and held in oven for 2h. Reactor is taken out and cooled down with a fan to room temperature. The solid particles and the liquid is separated by pouring the substances trough filter paper. The solvent is then analyzed in an GC/MS for any BFRs. The solid particles are air dried over the night and oxygen bomb combustion and ion chromatography analyzed for BFRs remaining in the plastic.

The process is resulting in the effect of temperature on bromine extraction. According to the results the amount of bromine in the solvent is increased with temperature below

90° and kept constant as the temperature increases. Naturally, the amount of bromine decreasing rapidly in the solid at 50° – 90°, as seen in figure 4.

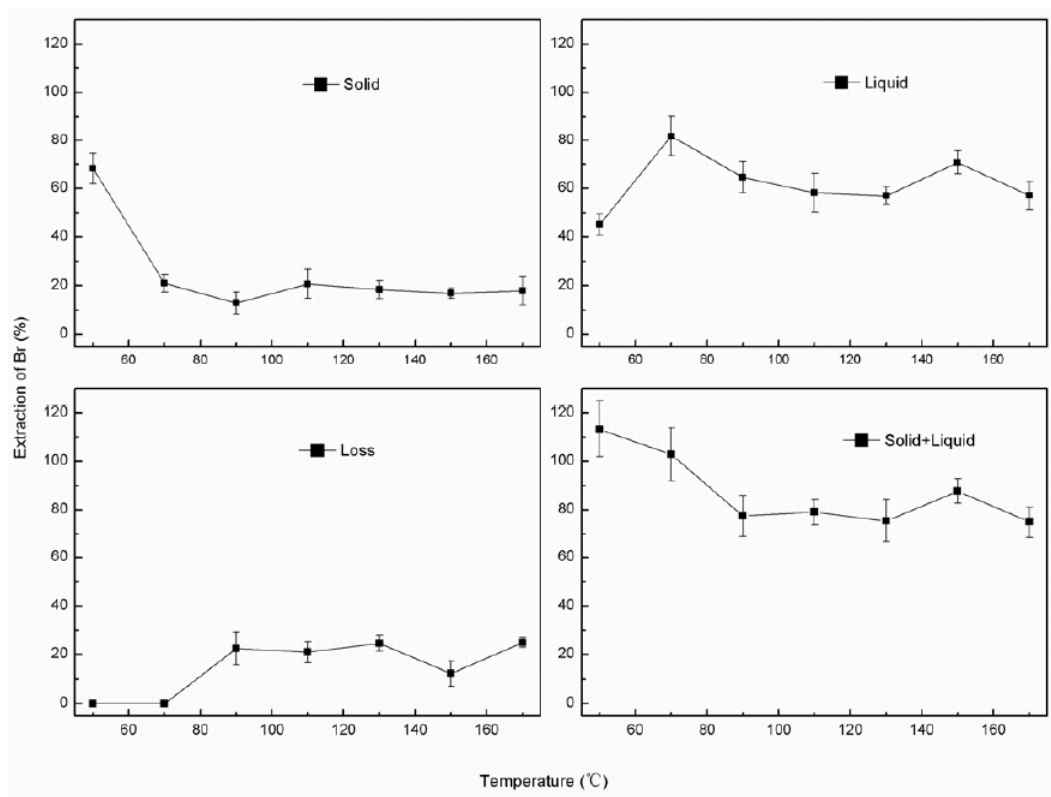


Figure 4 Effect of temperature on BFR extraction. (Zhang & Zhang, 2014)

The amount of bromine in the sample after the first 2 hours were reduced from the original 7.45% to 1.87% of the weight of the sample, see figure 5. After yet conditioning the sample a second time, with same parameters, there was no TBBPA left in the plastic. (Zhang & Zhang, 2014)

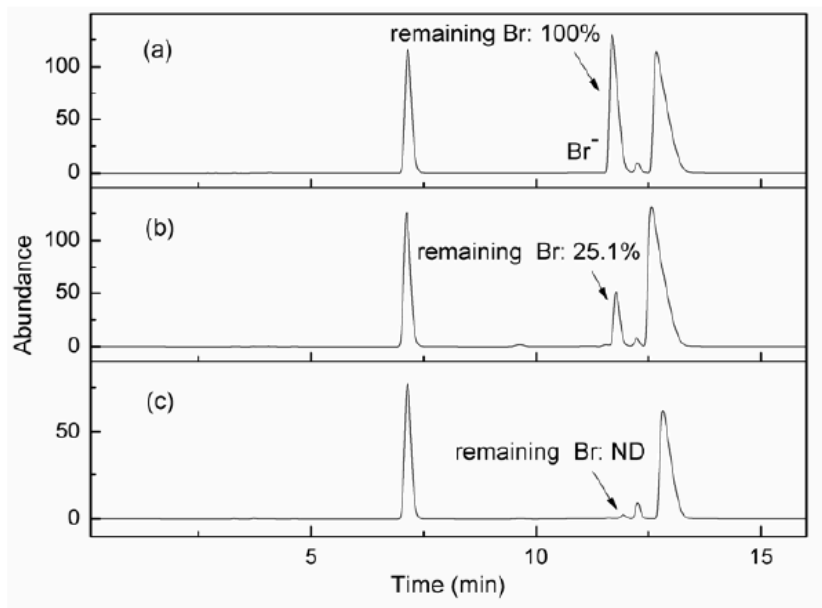


Figure 5. Ion chromatograms of plastic after a: no; b: once; c twice solvothermal treatments. (Zhang & Zhang, 2014)

In the solvothermal extraction article is used isopropanol as solvent. With a little further research in the topic a few articles were found testing out the most appropriate solvent for solvothermal treatment for BFRs.

A study made by Altwaiq et al. about extraction of BFRs from polymeric waste using different solvents and supercritical carbon dioxide was made in 2003. Four different extraction methods were performed; Supercritical Carbon Dioxide Extraction, SCDE with modifier, solvent extraction and soxhlet-extraction. The solvent extraction is further looked on since it is the method used for this research purposes. The solvents used are listed in table 5. (Altwaiq, et al., 2003)

Table 5. List of solvents and samples used for different materials in Altwaiq et al. research. (Altwaiq, et al., 2003)

List of samples and solvents used to extract the flame retardants with different extraction procedures

Sample	Extraction procedures		
	sc-CO ₂ + solvent after treatment	Modifier + sc-CO ₂	Solvent extraction
		Selected solvents	
ABS/TBBPA	Toluene	Toluene, 1-propanol, methanol	Toluene, 1-propanol, methanol
PS/TBBPA-dbp	Acetonitrile	Acetonitrile, 1-propanol, isooctane, methanol	Acetonitrile, 1-propanol
ABS-PC/TBBPA-ae	Toluene	Toluene, THF, 1-propanol	Toluene, THF + 1-propanol (3:1)
ABS/TBBPA-co	Toluene	Toluene, 1-propanol	Toluene, 1-propanol
ABS/TBPE	Toluene	Toluene, 1-propanol, methanol	Toluene, 1-propanol, methanol
PS-HI/HBCD	Toluene + 1-propanol (1:1)	Toluene + 1-propanol (1:1), methanol, acetonitrile	Toluene + 1-propanol (1:1), 1-propanol, methanol, acetonitrile
PS-HI/DECA	Toluene + 1-propanol (1:1)	Toluene + 1-propanol (1:1), 1-propanol, acetonitrile	Toluene + 1-propanol (1:1), 1-propanol, 1-heptanol, 2-octanol

The results from the solvent extraction were, that toluene was found to be the best solvent. TBBPA, TBBPA-co, TBPE efficiencies of about 100%. TBBPA-dbp solvent used acetonitrile best, efficiency of 93.8%. Extraction with 1-propanol and methanol shows relatively small success. In the extraction of TBBPA-ae, THF and 1-propanol (3:1) can dissolve PC, efficiency 73.8%, was used in order to suppress the solubility of the polymer sample. The efficiencies of extraction liquids are presented in the following figure, figure 6. (Altwaiq, et al., 2003)

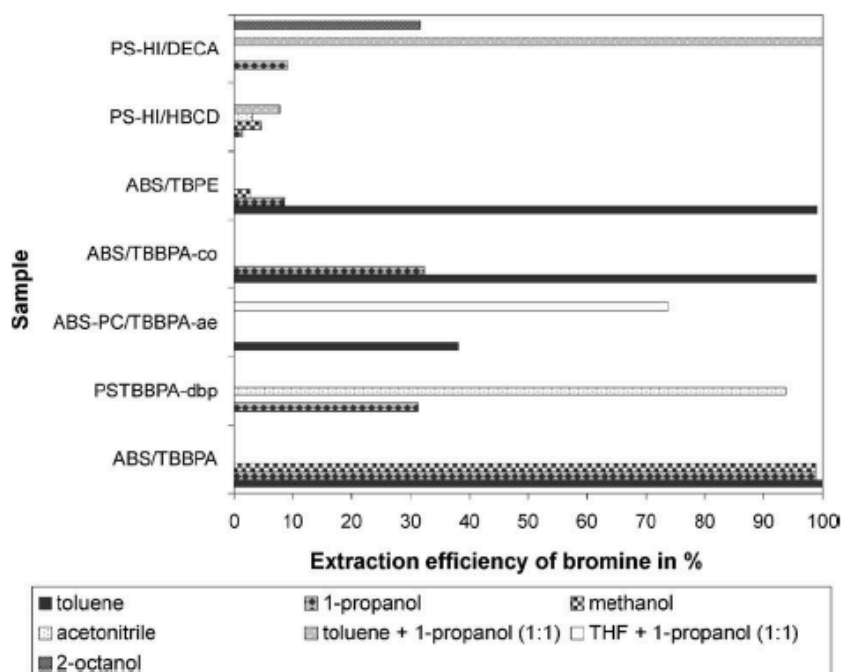


Figure 6. Extraction efficiencies of various solvents used in solvent extraction.

2.3.3 UV-Vis-NIR spectroscopy

UV-Vis-NIR spectroscopy, (Ultra-Violet, Visible, Near Infra Red spectroscopy), is used to analyze extracts, solid samples and define quantities of compounds in the matrix. The spectroscopy uses the ultraviolet to near infrared spectral region, about 200 nm to 3000 nm. The method is used to study interferences in the chemistry between electromagnetic radiation, molecules and atoms. The absorption of the light gives the energy of the electrons in molecules. Then by analyzing the absorption bands, the molecules and bonds present can be determined. (Bart, 2006)

The method is fast and is mainly used for quantitative determination of substances, in typically 0.1 to 0.2 mg samples, in analytical chemistry. Analysis of polymer films is limited because of unwanted light scattering from the polymers crystalline regions. (Bart, 2006)

The output is a graph of absorption (A) – wavelength in nm (λ), and uses the Beer-Lambert-law to compliance the concentration from the peaks in the graph. The Beer-Lambert-law states that the concentration is directly proportional to the absorbance of a solution as the sample thickness is known. Hence, the concentration can be determined by knowing how absorbance vary with concentration and then usage of tables of molar extinction coefficients or, determined from calibration curve. (Bart, 2006)

With UV-Vis-NIR spectroscopy a range of wavelengths can be selected for more accurate and precision results. In best case scenario the absorbance obtained during the measurement should be due to only the analyzed substance. However, Rayleigh and Tyndall scattering may interfere in the UV-Vis region that will have an affect on the results. The interferences reduce the accuracy of the analysis and gives a limited and poor selectivity of additives with similar absorbance. (Bart, 2006)

Additives that are heavily diluted with the polymer are poor to detect as the absorption bands of polymers and additives are overlapping. The only way to detect these additives are to hope for the polymer itself to have a relatively low absorption and the additive to show off sharp absorption bands. Impurities, like fillers and pigments may be absorbing

and interfering with the spectroscopy as well. To get around the problem with impurities, a solvent extraction can be used. (Bart, 2006)

Additives are often analyzed by extracting in solvents from the polymer matrix. The extraction method is a way to detect brominated flame retardants when analyzing with a UV-Vis-NIR. (Bart, 2006)

UV-Vis-NIR spectroscopy is the available method for this research so this method is to be used. As the UV-Vis-NIR is only capable of showing concentrations of substances, the method cannot confirm that any of the results showing is bromine. Samples will be prepared for the UV-Vis-NIR in form of extract liquids in cuvettes.

2.3.4 FTIR spectrometer

Fourier Transform Infrared Spectrometer (FTIR) is operating in the infrared region, About 750 nm to 1 mm. The method measures all infrared frequencies at the same time. Radiation in form of and interferometer produce a signal that is passed through a sample. A beamsplitter divides the beam onto two mirrors, whereas one of the mirrors is fixed and the other is moving. One beam will have a fixed length and the other constantly changing. The resulting signal is called interferogram, because of the beams interfering with each other.

The frequency spectrum coming through is interpreted using a Fourier transformation technique, where a computer calculates and presents the spectrum with Transmittance (%) – Wavenumber (cm^{-1}) table. The spectrum peaks are unique for every molecule structure and functional group, so this makes identification, quality and consistency of a sample possible. The procedure is demonstrated in the picture below, figure 7. (Thermo Fisher Scientific Inc., 2015)

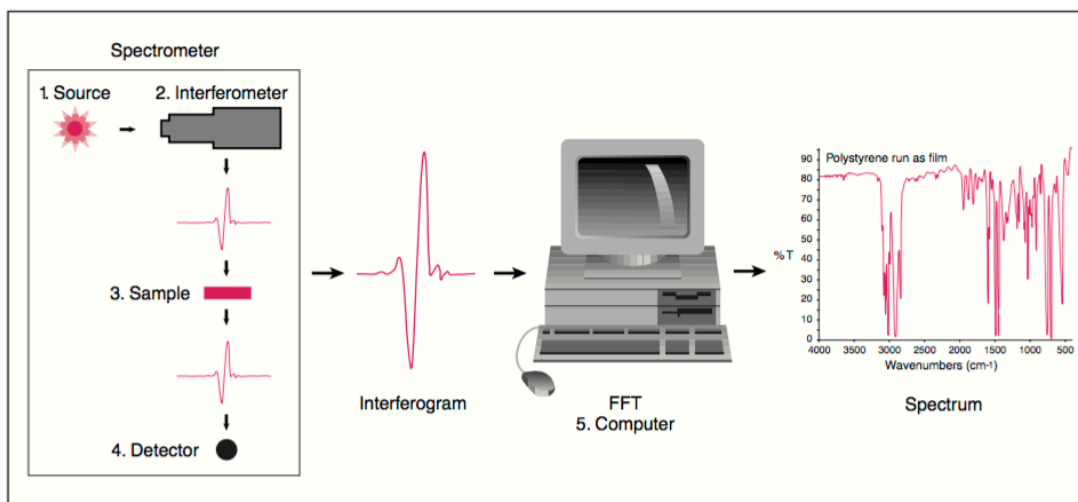


Figure 7 The FTIR analysis described in a picture. (Thermo Fisher Scientific Inc., 2015)

Advantages with FTIR, it is a non destructive method. It is fast, precise, mechanically simple, self calibrating and has a great optical output. Fellgetts' advantage result in information from all wavelengths are collected simultaneously which gives a higher signal to noise ratio in a scan. (Thermo Fisher Scientific Inc., 2015)

FTIR makes a great instrument for both quantitative and qualitative analyzes of additives. Bromine contents of more than 5% can rapidly and non destructively be measured with FTIR. For this paper a FTIR is used for identifying the plastic waste obtained for the research. (Burker Optics, 2016)

3 METHODS

A solvothermal process performed is done by Zhang & Zhang, 2014, in a research paper is going to be the base. In the original process isopropanol is used as solvent. Here, the solvent is changed to methanol since it was one of the solvents used in other research papers using the solvothermal process for extraction of BFRs, for example Altwaiq et al research. The process instructions are simplified as follows.

Equipment used in the process:

- Samples
- Grinder
- Reactor chamber
- Oven
- Filter paper
- Methanol

The process is performed as follows:

- Grind plastic samples to 1 mm particle size.
- Methanol and grinded plastics are added into the chamber. Liquid to solid ratio 12:1.
- Reactor is heated in oven to 90°C and held for 2 hours.
- Reactor is then cooled down quickly in refrigerator for 15 minutes.
- Liquid and solid is separated by the use of filter paper.
- Solvent is ready to be analysed.

3.1 Sample preparation

Samples were sent from Sweden, from a TV and monitor demolition line in Kumla. The plastic pieces received were five different TV or monitor pieces and people checked with a handheld detector that there is for sure bromine in the plastic. The samples were covered in dirt so the samples were washed with water to begin with. A picture, figure 8, was taken of the samples before grinded into usable pieces.



Figure 8. Plastic samples obtained. To the left washed and unwashed close-up of the surface to the right.

Samples were cut in smaller pieces and then grinded with a plastic scrap granulator of the brand Rapid, 15 series. The grinding plate 8 mm was used. The granulate size obtained varied from a couple of mm to tiny chips.

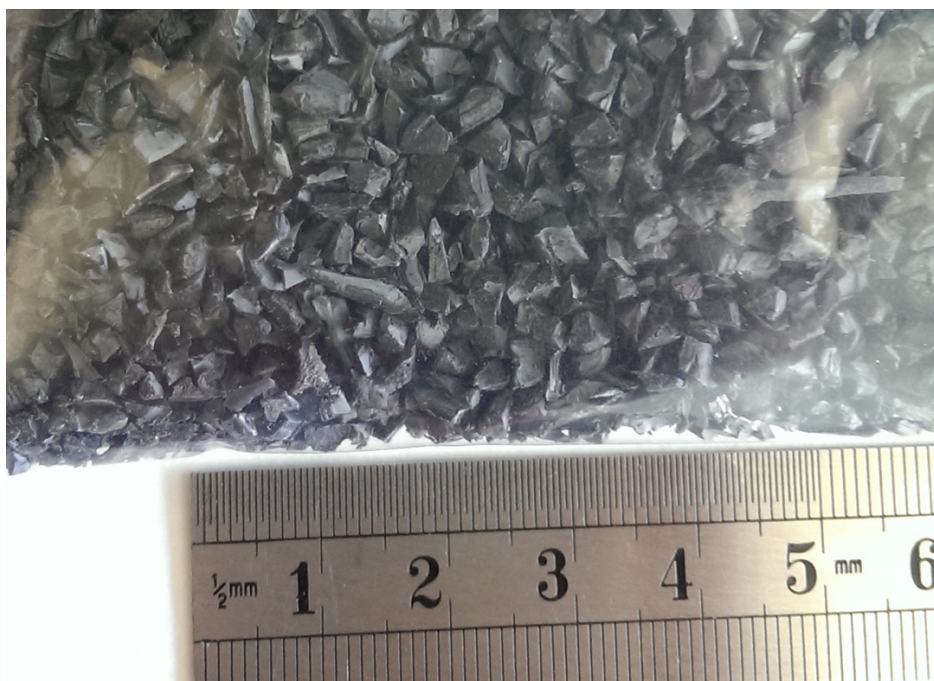


Figure 9. Size of achieved granulates.

The Received amounts of granulates of each plastic sample are plotted in the graph below.

Table 6. Weight of the sample before and after grinding.

Samples	Weight, Sample (g)	Weight, Grinded (g)
1	95.67	72.39
2	70.64	55.64
3	41.08	30.46
4	51.36	43.37
5	91.09	76.48

3.2 Extraction setup

The setup was consisting of two reactor chambers, both holding 3 ml. Two specimen could be made at a time and out of each sample was extracted four specimens. The chamber itself is out of PTFE with two sealing rings keeping it tight and under pressure, making it a reactor chamber. A ETFE sheet is put on top and fixed with a lid-like cover, which is tightened with bolts. Figure 10 to the left is demonstrating the setup below.

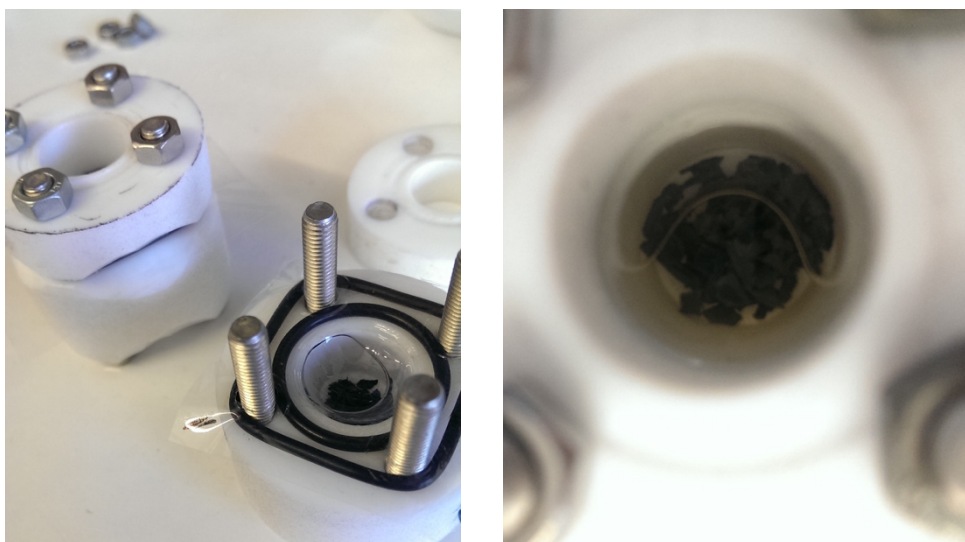


Figure 10. Reactor chamber setup to the left and chamber after 2 hours in oven to the right.

The reactor is put two hours in the oven with the methanol and plastic inside. The decided plastic to solid ratio is 12:1. Methanol is placed in the beaker and afterwards the reactor is put to cool down in the freezer of -28°C for 15 minutes. The results can be seen in figure 10 to the right. The next step is filtration and separation of the extract from the solid. VWE qualitative filter paper, 417, is used for the filtration. The filtration is done with a pipette and a filter paper straight into a glass specimen jar, which is then put in the fridge for preservation. The filter paper is wetted with pure methanol before filtration so that the small amounts of extract will not all be sucked up by the paper. The chosen particle penetration size is $40\ \mu\text{m}$, because of the filtration is only supposed to separate the solid plastic from the extract. A schematic view of the process from solid sample to extract is shown on the next page, figure 11.

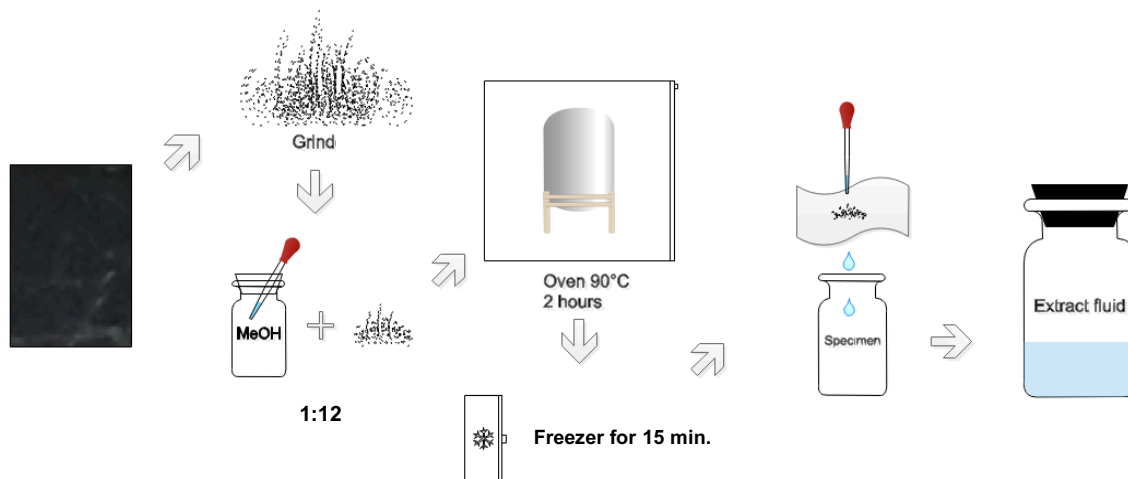


Figure 11. The steps from solid part to extract fluid.

3.2.1 Identification of plastic samples and extracts

The plastic and the extract samples are analyzed in different ways. The extract fluid is analyzed with UV-Vis-NIR and the plastic granules are analyzed with an FTIR. A schematic view below in figure 12 is demonstrating the analysis.

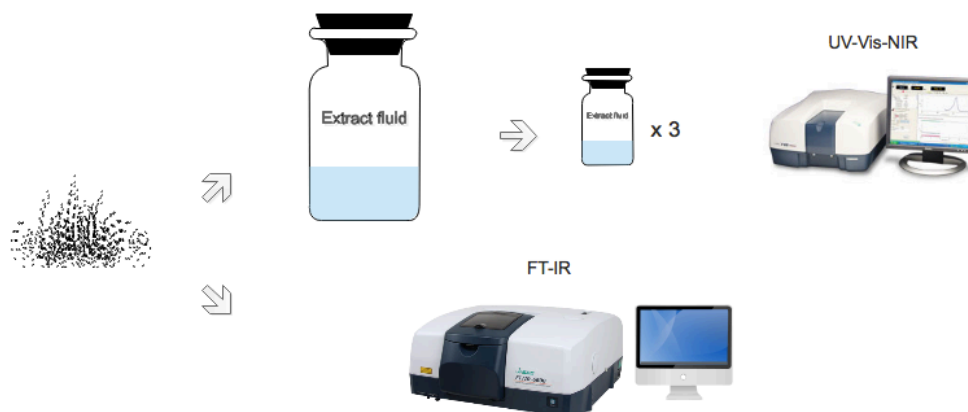


Figure 12. Schematic view of analyzing of the samples.

The identification of the plastic is done with an FTIR, Spectrum One FTIR spectrometer – PerkinElmer, in the laboratory of Helsinki University. A tiny flake of the plastic is put under the measurement eye and the FTIR gives a spectra of the analyzed material. The spectra are compared with the FTIR software library and lists the highest matching substances with similar spectra. All five original plastics are identified.



Figure 13. FTIR spectrometer at Helsinki University.

The extract liquids are analyzed with an UV-Vis-NIR, Jasco V-670, at Arcada. Since the UV-Vis-NIR is only capable of showing concentrations of substances, identification of an unknown substance cannot be done. A baseline is created with an empty cuvette. The following substances are measured; Methanol, H₂O (distilled), Methanol + Bromine mixture and the extracts made. Methanol, H₂O and a Methanol + bromine mixture are used as references for analyzing the extract samples. The parameters used was 400 nm/min scanning speed with a medium response and 0.5 nm data interval. UV-Vis bandwidth is set to 2 nm and NIR bandwidth 4 nm. The different substances' outputs are compared with each other for elimination of as much as possible unknown factors from the sample spectra.

3.2.2 Failure modes

Several trials in the beginning did not give any results. There was encountered three problems, (1) rubber seals being old and brittle, (2) ETFE film bursting because of too much pressure and (3) reactor was not tightened enough and letting the methanol escape.

The process was not working at first because of rubber seals being old and cracking. It resulted in methanol escaping in form of vapor from the chamber since the oven was 90°C and methanol has a boiling point of 64.7°C. In the evaporated chamber could clearly be seen brownish remains on the edges after removing the plastic granolas.



Figure 14. Brownish remains of a failed evaporated chamber, plastic has been removed (to the left) and cracking seals to the right.

The remains in the chamber was tried to soak in methanol for 40 minutes in the hope for it to be bromine, but did not reveal anything in the UV-Vis-NIR spectra. However, new seals were ordered and the problem with escaping methanol vapor was fixed.

Another failure encountered was the pressure being to high and causing the ETFE film to burst. The ETFE films could be re-used a couple of times and then the films did not hold anymore. A picture below is showing a bursted ETFE film. Obviously the bursted film caused the methanol to escape from the chamber.



Figure 15. Bursting ETFE film.

The third problem encountered was the methanol escaping from the chamber without any visual problems. This caused probably by uneven tightening of the bolts, wrinkles in the ETFE film or dust or other dirt on the seals causing a little gap to let the methanol out.

4 RESULTS

The extracted samples obtained were visually changed from pure methanol. A slight yellow tint to the clear methanol was obtained. Bromine are usually described as brown substance so based on this the solvents looked promising. However, all the plastics were colored in a black or gray shade, which would indicate that there has been used additives for coloring. The discoloring is visually appearing best in the black colored plastics, sample 1 and 4, nevertheless every sample had a slight tint. A picture below demonstrating the discoloring of the extract. A granulate of each sample is placed in front of representing extract for demonstration of the color of the plastic. Appendix A in the end is showing each extraction attempt with specific data.

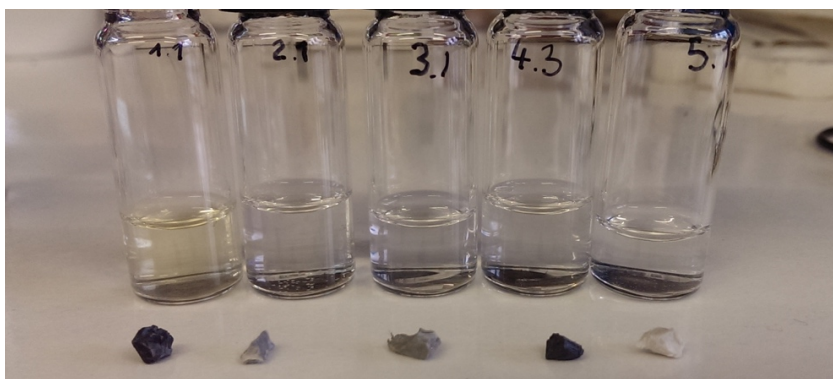


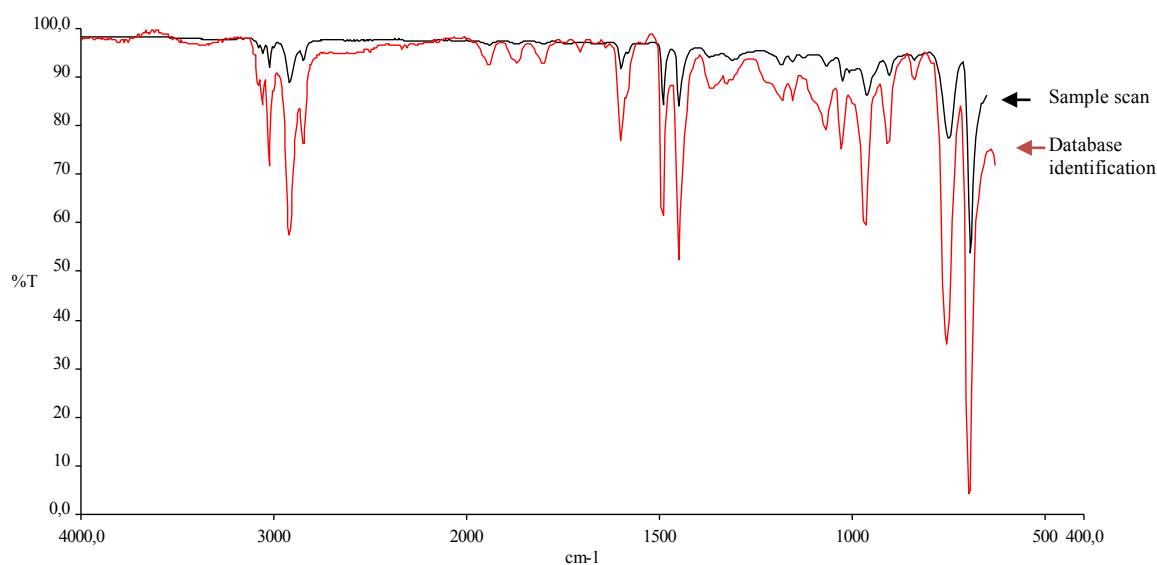
Figure 16. Discoloring of the extract in each sample.

4.1 FTIR results

The plastic grinded into five batches was identified with a FTIR. The results from the FTIR shows that samples 1 – 4 are styrene/butadiene copolymer with 85% styrene. The FTIRs materials library was highly suggesting for all samples 1 – 4 simple styrene. The spectra for styrene and the sample spectra appeared however not to be matching with some peaks when comparing them to each other, therefore the material was decided to be more matching with styrene/butadiene copolymer with 85% styrene. Also, computer and TV-housings would not be made out of brittle 100% styrene, hence the second reason for the material to be a styrene/butadiene copolymer.

Sample five appears to be polycarbonate, which gave best matching percentage of the suggested materials from the computer materials library. Polycarbonate is a likely material for a TV or computer-housing and therefore decided to be polycarbonate.

The following spectrums are gathered from the data obtained from the FTIR. Black lines are representing the analyzed material and red line is the highest match acquired from the software library. Vertical axis represents the transmittance in percent and horizontal axis is the wavenumber in cm^{-1} .



X

Figure 17. Sample 1. Identification styrene/Butadiene copolymer 85% styrene. Sample scan black line, database identification red line.

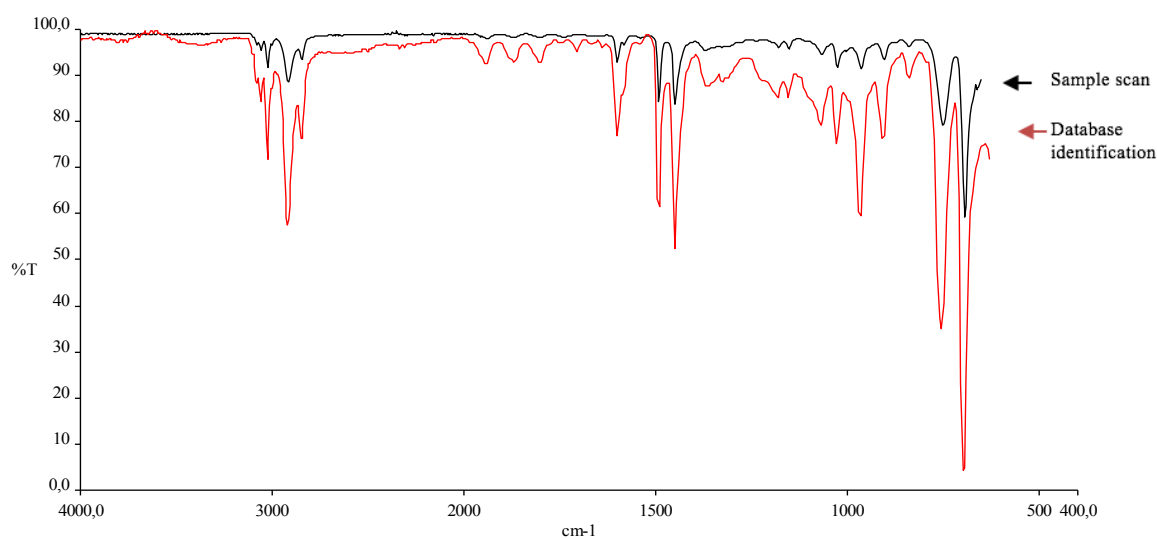


Figure 18. Sample 2. Identification styrene/Butadiene copolymer 85% styrene. Sample scan black line, database identification red line.

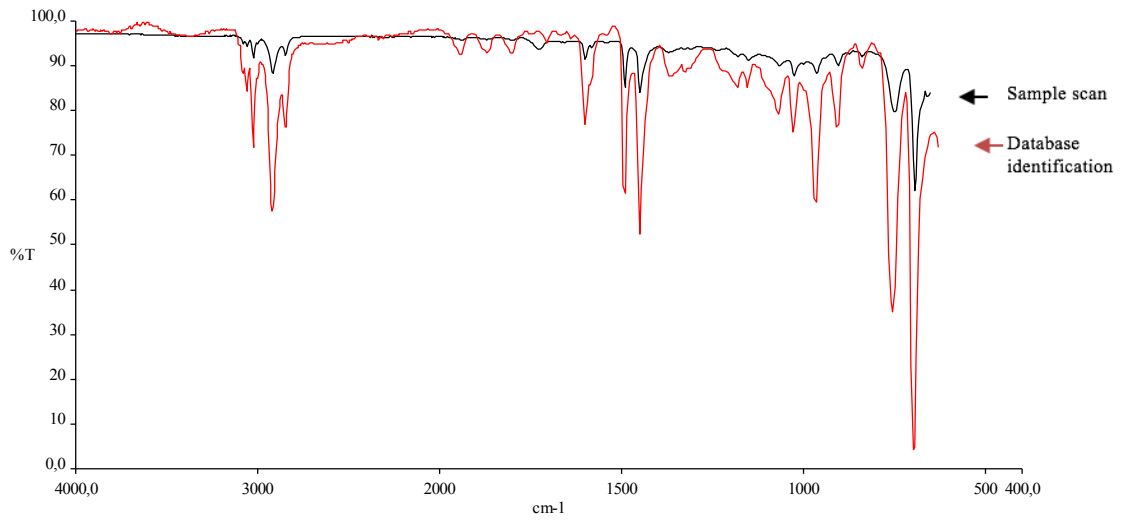


Figure 19. Sample 3. Identification styrene/butadiene copolymer 85% styrene. Sample scan black line, database identification red line.

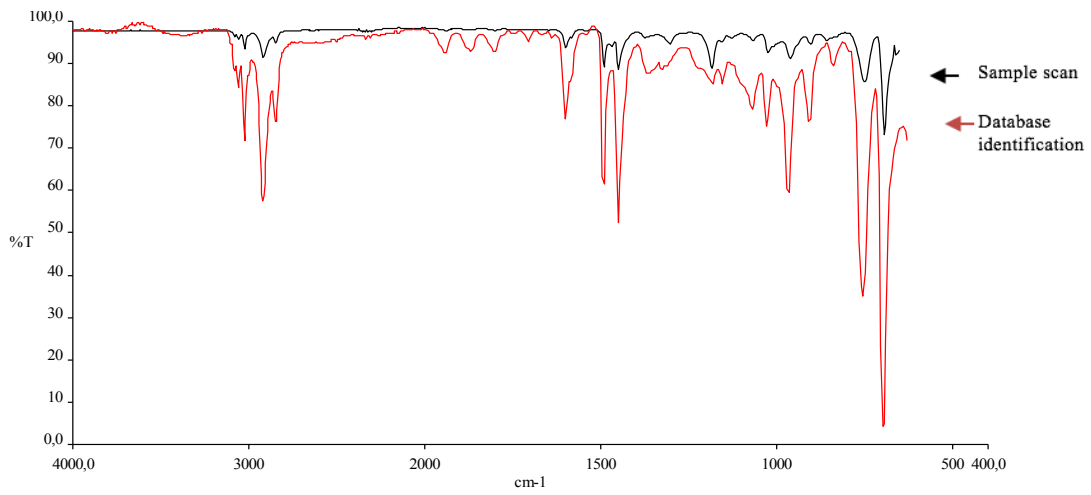


Figure 20. Sample 4. Identification styrene/butadiene copolymer 85% styrene. Sample scan black line, database identification red line.

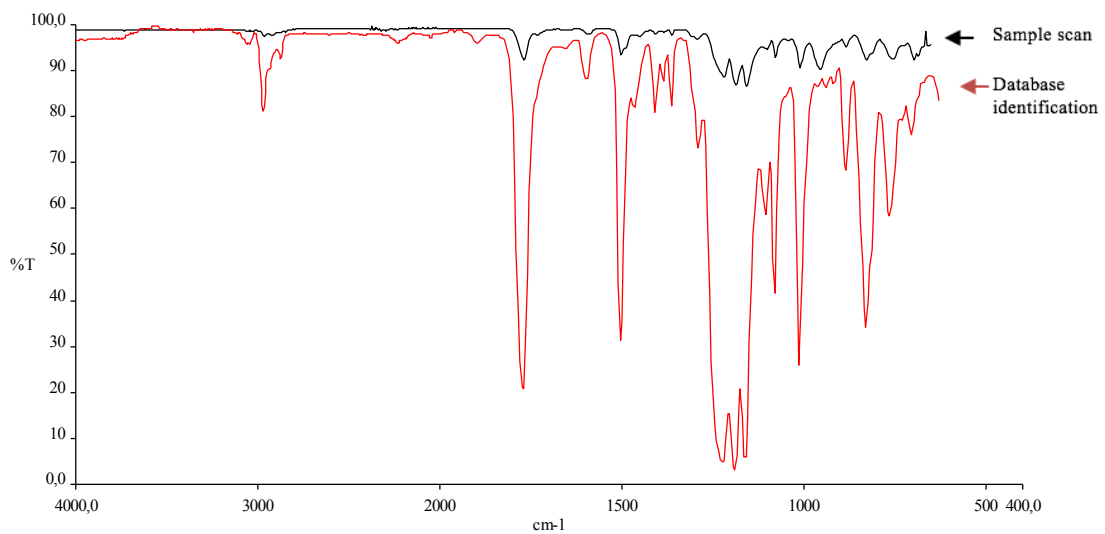


Figure 21. Sample 5. Identification polycarbonate. Sample scan black line, database identification red line.

4.2 UV-Vis-NIR results

Baseline is first created with an empty cuvette. References are made to compare the extract spectra to be able to determine if there is a possibility of bromine being present. A spectra of the most expected substances in the extracts, the references, are analyzed for removing as many of unknown factors as possible. A scan of each reference sample is merged into one graph resulting in figure 22. The spectrum is displayed from 1400 nm – 200 nm since above 1400 nm was appearing terribly much noise. Since the results of a UV-Vis-NIR does not work for determining unknown substances, the method of identification has to be made on assumptions and comparison of known substances.

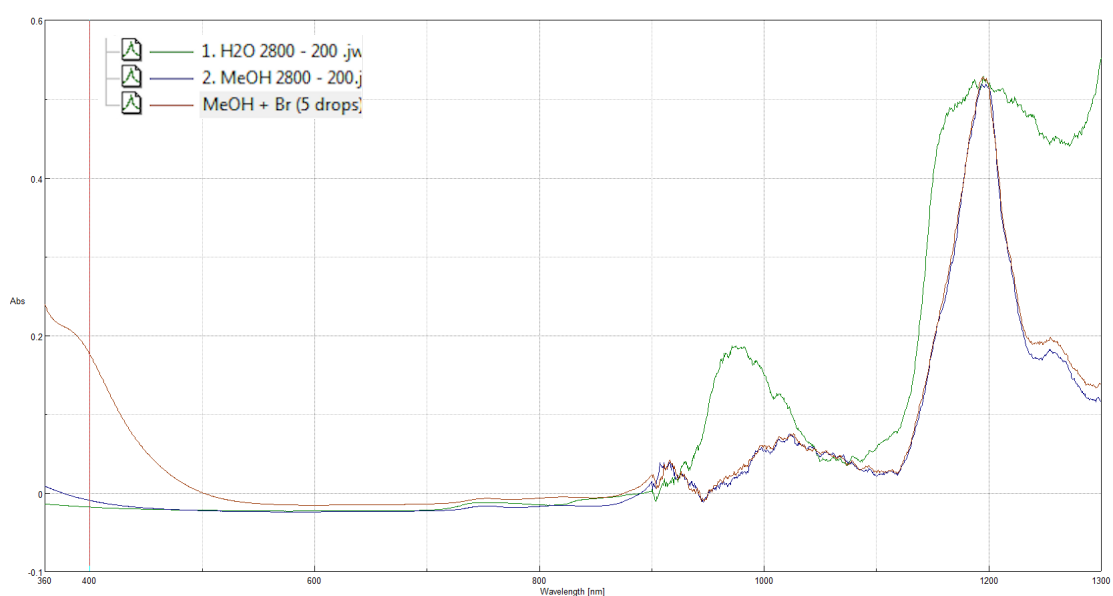


Figure 22. A graph showing the spectra of H₂O, MeOH and MeOH + Bromine graph.

In the graph can be seen a spectrum for H₂O in green, MeOH in blue and MeOH - Bromine mixture in brown. The green H₂O spectra is clearly standing out from the blue and brown. Green and brown are following quite the same path except for in the 500 – 200 nm region, which indicates that bromine could appear in the MeOH + bromine spectrum in this region.

Methanol is the major part in the extract, and it is therefore used as one reference samples. Water is highly probable to be present in mixture, therefore distilled water. Bromine is mixed with methanol to compare pure MeOH with MeOH + Br mixture. MeOH + Br is mixed in different ratios for analysis of samples. The different ratios are consisting of always 4 ml MeOH and then added 1, 2, 5 and 10 drops of Br solution of 1%.

The samples were then scanned and the following results were obtained and represented in figures 22 to 26. Three extract samples are chosen to be scanned out of the four original extract samples of each plastic type. Since not all samples were containing the same amounts of solvent, some were too little to be analyzed. In the 4th sample, only two of the samples were enough to fill up the necessary amount in the cuvette for analysis.

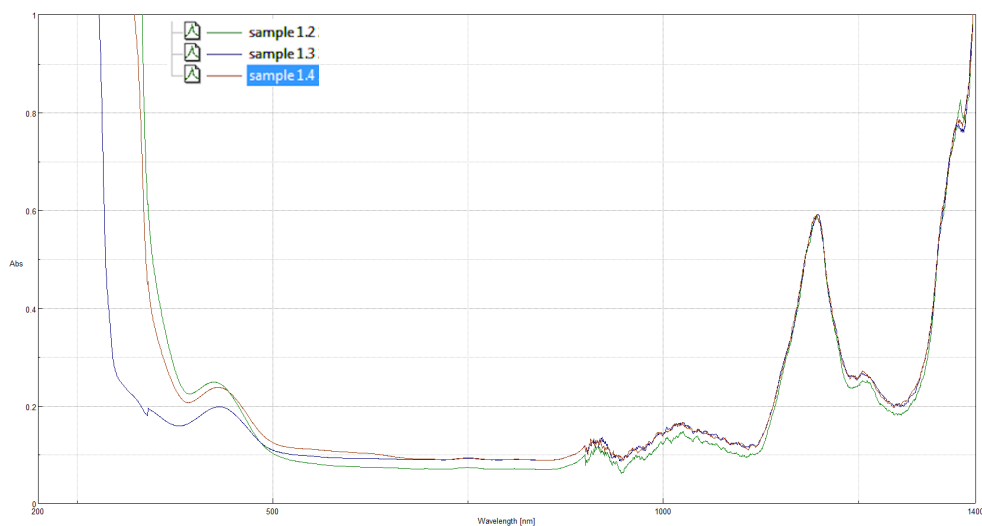


Figure 23. Sample 1, batches 1.2, 1.3, 1.4 merged.

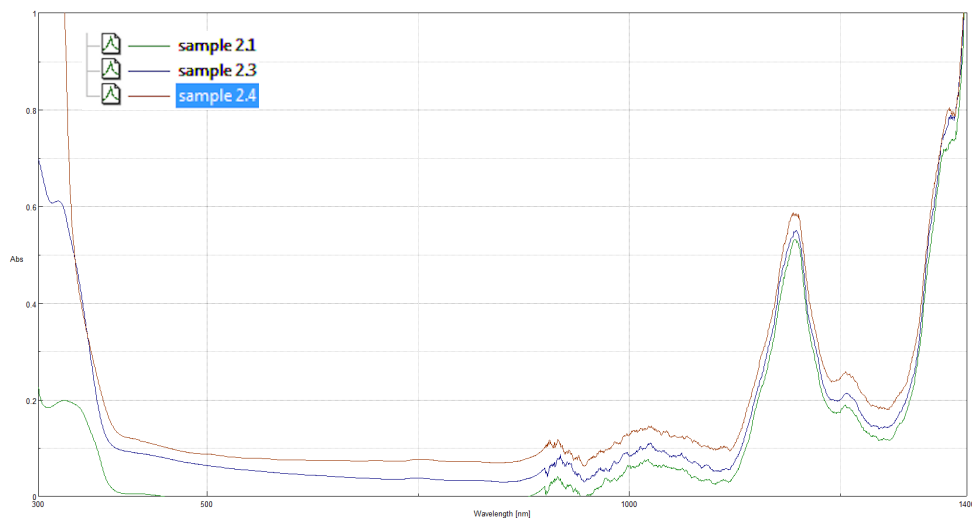


Figure 24. Sample 2, batches 2.1, 2.3, 2.4 merged.

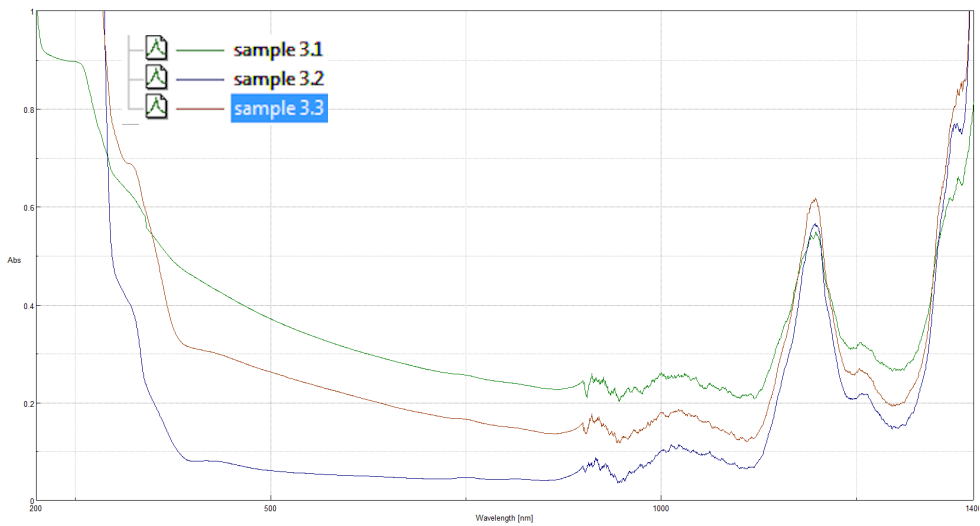


Figure 25. Sample 3, batches 3.1, 3.2, 3.3 merged.

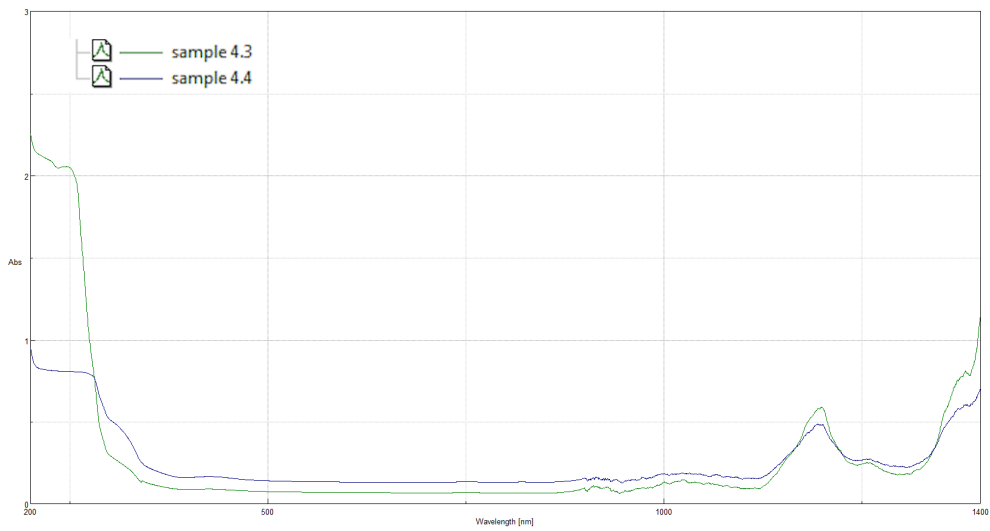


Figure 26. Sample 4, batches 4.3, 4.4 merged.

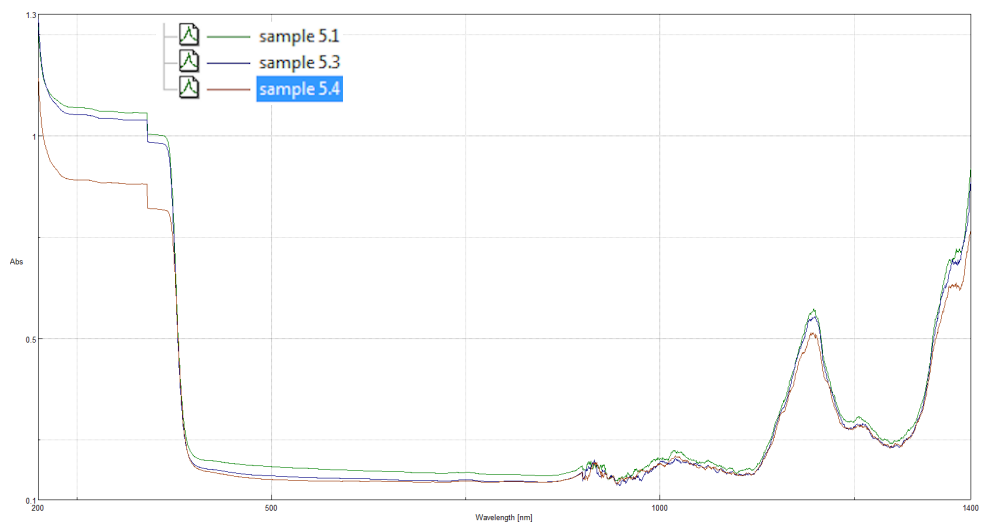


Figure 27. Sample 5, batches 5.1, 5.3, 5.4 merged.

It is evident from all the samples that they have in common the same peak pattern from 1400 nm – 500 nm, as seen in MeOH and MeOH + Br reference samples. Therefore, it can be concluded that these peaks are characteristic for methanol. The most interesting part is 500 nm – 200 nm. In this region can be seen changes in the different sample spectras. It is also where the rays come into the ultraviolet wavelengths, and therefore the readings are not so accurate. However, samples appear to have a peak appearing in this region, that is not present in either H₂O nor MeOH spectras. The following figure 28 gives a closer look at 500 nm – 200 nm.

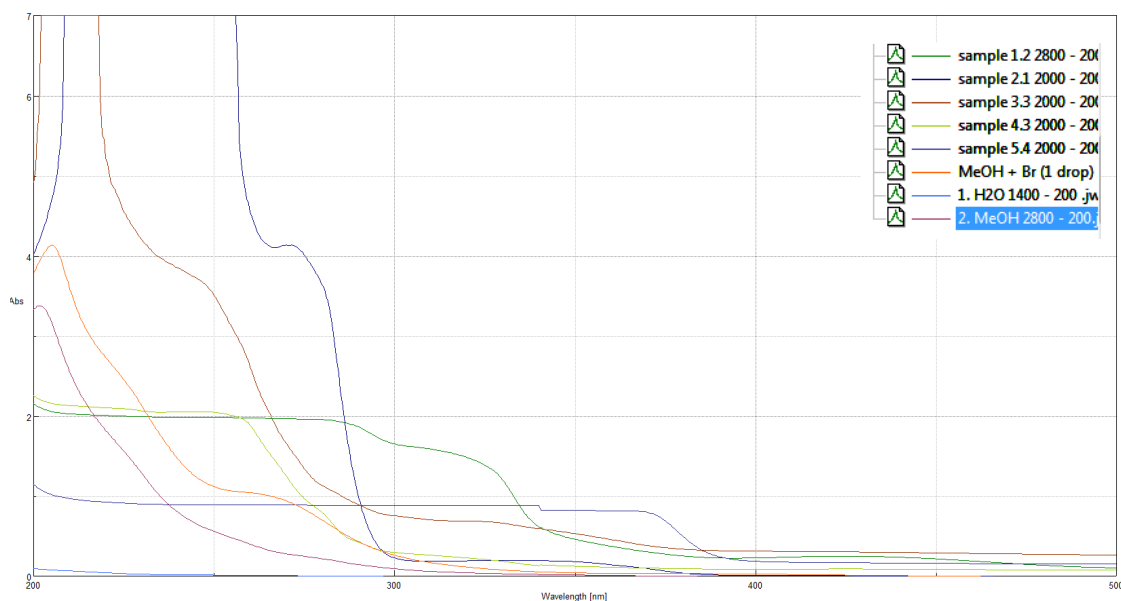


Figure 28. Reference samples and test samples 1 – 5 all merged in one graph.

In figure 28 is merged all the reference and test samples from a spectrum of 500 nm to 200 nm. The range from 400 nm – 250 nm shows in all of the samples 1 – 5 a little peak or bump, that is not showing in the MeOH nor H₂O spectra. This would indicate that there could be a little of bromine showing up. The small peaks assumed to be bromine are presented in figure 29. However, bromine present in the plastic and pure bromine could show up and give different readings for the UV-Vis-NIR scan. The type of covalent binding is not the same in Br-Br and bromine-hydrocarbon compounds.

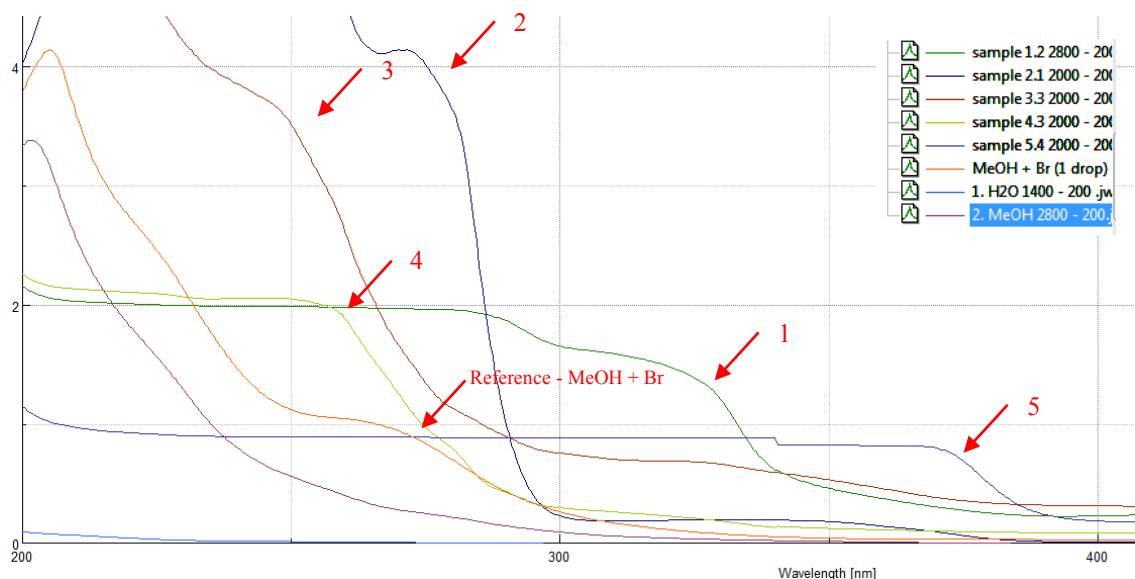


Figure 29. Peaks that appears to be bromine in the extracts marked with red arrows.

In the research, “Extraction of BFRs from polymeric waste material using different solvents and supercritical carbon dioxide”, by Altwaiq et al, table 7 was found and is listing typical functional groups of brominated flame retardants with wavelengths where they should appear.

Table 7. Typical functional groups and their frequency range.

The characteristic infrared bands of relevant brominated flame retardants	
Functional group	Frequency range (cm ⁻¹)
δ (Alkyl-Br)	680–515
δ (Aryl-Br)	1075–1030
ν (C=C aromatic)	1600–1500
ν (Aryl-H)	3100–3000
δ (substitution patterns of the benzene ring)	840–700
δ (C(CH ₃) ₂)	1395–1365
ν (OH)	3600–3200
ν (O=C=O)	2340
ν (O-CH ₂ O-O)	2790–2970
δ (CO-OH)	1250–1000
δ (CO-OO-C)	1275–1200

The functional groups that could be present beneath noise and not showing up in the spectrum are; C=C aromatic 1600 – 1500 nm and C(CH₃)₂ 1395 – 1365 nm. The possibility of carbon black being used as pigment for the black plastic is something to take into consideration. Carbon black appears to have ketone and carbonyl groups, which appear in wavelengths from 1820 – 1670 nm and 1725 – 1705 nm. The carbonyl groups cover pretty much everything of the noisy area. In the table is displayed functional groups from the infrared region, which means the peaks at lower wavelengths are not concluded.

5 DISCUSSION

One of the purposes of this thesis was to try out a simple solvothermal method based on an existing paper. The method tested was interesting because of the simplicity of the process compared with a lot of other researches done in the field of extracting of brominated flame retardants. The process itself worked well, a reactor chamber of PTFE was made with boiling methanol with ground samples and extract solvents were successfully obtained.

The results from the plastic identification tells that samples 1 – 4 are polystyrene and sample 5 being polycarbonate. According to the literature review, polystyrene would most likely contain Octa-BDE. Brominated polycarbonate would most probably be Octa-BDE, Penta-BDE and PBB, but these substances have been phased out in Europe.

The solvent was changed to methanol, from the original isopropanol, appeared not to be the best option because of figure 6 on page 32, Altwaiq et al. In the figure can be seen high impact polystyrene, HI-PS, containing Deca-BDE where methanol shows zero efficiency, HI-PS containing HBCD shows about 7% efficiency. Polycarbonate is not listed in the table. According to the research toluene would have been the best choice for extraction of BFRs. However, methanol was chosen because the molecule being similar to the isopropanol that was originally used in the research.

Using UV-Vis-NIR for determining bromine in the extracted sample is not the most reliable way to confirm BFRs existence in the solvent. Results are based on assumptions that the absorption peaks appearing outside of the reference samples in the spectra are bromine. The assumption is made on the facts that the extraction process works, and there should theoretically be bromine in the extracted sample. For getting the best analysis of the extract another analysis method such as CG/MS should be used to properly identify the substances present in the solvent.

6 CONCLUSIONS

From the literature review can be concluded that 9 million metric tons of electric and electronic equipment is placed on the market in the EU each year. In figure 1 on page 14, can be concluded that most of the gathered 3.5 million metric tons of waste is ending up as recycled and for energy recovery. The amounts of non gathered EEE waste are still massive, and would require a lot more effort for gathering of the waste in the future. The WEEE Directive - Directive 2012/19/EU, is making goals and minimum limits for gathering of WEEE for the future and more waste should be gathered each year.

The wanted output of the experimental review was to see bromine appearing in the spectra of the sample analyzed with a UV-Vis-NIR. The results of the extraction are not the most reliable as stated in discussions section as it is based on assumptions. As reference samples are used substances that are for sure existing in the extracted samples, so MeOH, MeOH + Br and H₂O are analyzed with UV-Vis-NIR as well. The samples are compared with the references and therefore can be concluded that all remaining peaks that are not present in the references, are bromine.

Samples are compared to references and in figure 29. Each different sample appear to all have in common the somewhat weak extra peak in the range from 400 nm – 350 nm, that is not seen in pure methanol spectrum. The spectra are also similar to the methanol + bromine mixture spectra, which would indicate it to be bromine. H₂O was added as reference because of water always being present in substances, but it is concluded to not be showing up remarkably in the extract samples.

However, the methanol and bromine mixture is made with pure bromine, which means bromine is having Br-Br covalent bindings. The bromine assumed to be present in the extracted liquid might have different form and bindings, which a UV-Vis-NIR would make it show up on different wavelengths. The MeOH + Br is however appearing to be similar to the extract spectrum as extracted samples. Therefore, it is concluded that the liquid extraction is working and bromine was found to be in all of the extracted samples.

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APPENDIX

Appendix A – Extraction attempts

Sample Nr.	Solid weight (g)	Solvent volume (ml)	Liquid to solid ratio	Fail/Success	Comments
1.1.1	0.2386	2.5	1:11.9	Fail	Dry, Bad seals
1.1.2	0.2356	2.5	1:11.8	Fail	Dry, Bad seals
1.1.3	0.2366		1:11.8	Fail	Dry, Bad seals. Attempt to soak up brown remains from the reactor, Fail.
1.1	0.2378	2.5	1:11.9	Success	New seals. Slight yellow color solvent.
1.2	0.2375	2.5	1:11.9	Success	Slight yellow color solvent.
1.3	0.2377	2.5	1:11.9	Success	Slight yellow color solvent.
1.4	0.2372	2.5	1:11.9	Success	Slight yellow color solvent.
2.1	0.2383	2.5	1:11.9	Success	Forgot to change filtration filter between plastic samples. Might have a few extra drops of MeOH. Very weak yellow tint in color.
2.2	0.2376	2.5	1:11.9	Success	Very weak yellow tint in color.
2.3	0.2380	2.5	1:11.9	Fail	A plastic piece fell on the floor. ETFE film bursted.
2.4	0.2376	2.5	1:11.9	Success	Very weak yellow tint in color.
3.1	0.2377	2.5	1:11.9	Success	Forgot to change new filter between plastic samples.
3.2	0.2373	2.5	1:11.9	Fail	MeOH evaporated. Maybe dirt on the seals.
3.3	0.2377	2.5	1:11.9	Success	Very weak yellow tint in color.

3.4	0.2372	2.5	1:11.9	Success	Very weak yellow tint in color.
4.1	0.2377	2.5	1:11.9	Success	MeOH evaporated to about half its volume. Bolt not tightened enough? Very weak yellow tint in color.
4.2	0.2384	2.5	1:11.9	Success	MeOH evaporated to about half its volume. Bolts not tightened enough? Very weak yellow tint in color.
4.3	0.2384	2.5	1:11.9	Success	Very weak yellow tint in color.
4.4	0.2370	2.5	1:11.9	Success	Very weak yellow tint in color.
5.1	0.2383	2.5	1:11.9	Success	No color at all.
5.2	0.2374	2.5	1:11.9	Success	No color at all.
5.3	0.2372	2.5	1:11.9	Fail	Very little MeOH left, Everything sucked up by the filter.
5.4	0.2373	2.5	1:11.9	Success	No color at all.
2.3 New	0.2372	2.5	1:11.9	Success	Very weak yellow tint in color.
3.2 New	0.2386	2.5	1:11.9	Fail	Dry, may have been dirt on the seals.
3.2 New 2	0.2382	2.5	1:11.9	Success	Very weak yellow tint in color.