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Brominated Flame Retardant (BFR) Reduction in Plastics from Electronic and Electric Equipment Waste
(WEEE)

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Abstract

Brominated flame retardants (BFRs) are additives used in plastics to prevent electronic and electric equipment from setting fire. The most commonly used BFRs today include tetrabromobisphenol A (TBBPA), hexabromocyclododecane (HBCD), and various polybrominated diphenyl ethers (PBDEs) [17]. BFRs are known to bioaccumulate and have caused harmful health effects, including interference of brain and skeletal development in animals [8]. When incinerated at low temperatures in the presence of oxygen, brominated dibenzo-p-dioxins are produced, also believed to pose toxic threats to the environment [18].

The lack of adequate handling of the e-waste generated worldwide as the technology boom continues has led to novel research in improving the recycling and disposal of plastics containing these additives. Soxhlet extraction (SE) is one of many extraction methods currently being researched to extract BFRs prior to decomposition of the waste. An industrially viable method to decomposing the plastics while reducing the formation of these brominated dioxins is pyrolysis, a thermal process in the absence of oxygen. We anticipate to find that utilizing SE on various brominated plastic fractions will result in lowered levels of brominated flame retardants after pyrolysis than those fractions which did not undergo SE.

1.0 Introduction

1.1 Defining e-waste and its presence

Electronic and electrical equipment waste, or e-waste, is any device disposed of by a user that runs on batteries or requires an outlet. These items range from portable devices such as cell phones or laptops, to large household items, including refrigerators, televisions, etc.

E-waste is mixture of several materials such as metals, plastics and ceramics. E-waste is also composed of hazardous materials such as mercury, lead and nickel, and precious metals including platinum, palladium, and gold. E-waste also comprises 21% plastics by weight [16], ranging in usage from device casings to PC-Boards.

Globally, the amount of electronic and electrical equipment produced by the industry has grown from 33.8 Mt (million tonnes) in 2010 to 41.8 Mt in 2014, with projections close to 50 Mt in 2018 [3]. Eurostat also released in 2012 a growth rate of e-waste by three to five percent annually [9], indicating that the generation of this waste is not subsiding any time soon. This coincides with the ever-increasing competition within the technology industry to make faster and better products for users, decreasing the lifespan of today's technology. The industry's generation of EEE isn't as concerning as is the lack of sophisticated growth of the e-waste system worldwide in conjunction with this technology boom.

Table 1 gives worldwide e-waste generation, along with highlights of countries with the highest contributions.

Table 1. E-waste generation worldwide. Countries with highest e-waste contributed is also shown (United Nations University, 2014).

Region	Countries with highest e-waste generation	E-waste generated, Mt	Total E-waste generated, Million tonnes (Mt)
Africa			1.9
	South Africa	0.35	
	Nigeria	0.22	
	Egypt	0.37	
Americas			11.7
	United States	7.1	
	Brazil	1.4	
	Mexico	1	
Asia			16
	China	6.0	
	Japan	2.2	
	India	1.7	
Europe			11.6
	Germany	1.8	
	United Kingdom	1.5	
	France	1.4	
	Russia	1.2	
Oceania			0.6
	Australia	0.47	
	New Zealand	0.09	
	Papua New Guinea	0.0008	

1.2 Brominated Flame Retardants (BFRs)

To prevent EEE devices from setting fire, flame retarded epoxy resins are added to the plastic casings, such as tetrabromobisphenol-A (TBBPA), hexabromocyclododecane (HBCD), and various

polybrominated diphenyl ethers (PBDEs). BFRs release bromine as free radicals to bond with other free radicals, and as a result reduce the chances of flame formation by bonding to molecules that would otherwise have caused flames to spread [10]. Chlorine is another halogen once used in flame retardants, such as polychlorinated biphenyls (PCBs) and polychlorinated naphthalenes (PCNs). Since the discovery of the harmful effects of these flame retardants though, many have been banned, but still persist in harming today's environment from devices of older generations [2].

When plastic waste from EEE is incinerated in the presence of oxygen at relatively low temperatures for long periods of time, reactions between the BFRs and combustion cause dioxins to be released into the atmosphere [15]. These dioxins have been known to cause harmful health effects, such as interference of brain and skeletal development in animals [8].

1.3 Disposal and Concerns

The western region of Africa currently does not have regulations in place on its e-waste disposal as rigorous as the rest of the continent, and therefore frequently receives e-waste from nations around the world. In Central and South America, only 6 countries have at minimum national laws pending approval, while the US and Canada have state-level and province-level laws, respectively. However, it should be noted that the United States still has not ratified the Basel Convention, an international agreement which restricts the international movement of e-waste and other hazardous waste to developing nations [5].

Though some countries such as Ethiopia show e-waste generation which aligns with the country's use of electronic devices, not all of the regions' reported numbers reflect the same story [3]. With developing countries such as China and western Africa still lacking enforced laws in the informal sector for the handling of e-waste, they often become a solution for developed nations to dump their own unwanted e-waste to be dealt with there. As imagined, these informal sectors have unsafe working conditions and many reusable parts are not recycled. Workers dismantle the various devices by hand or with rudimentary tools, and often burn much of the products in open fires to extract metals such as copper, or extract precious metals such as gold from chips in circuit boards via acid baths. Workers often don't have any form of protection from inhaling the toxic fumes, and/or work in enclosed spaces. Melting of plastic parts, e.g. device casings or printed circuit boards, are also done in this manner [4].

There are currently recycling facilities that have dismantled WEEE and used processed waste for partial self sustainability. The WEEE plastics are combined with these metal fractions of e-waste and processed via a pyrometallurgical treatment, originally for extracting metal to be further refined later. This involves an integrated smelter, a smelter with added functionality to handle plastics. These integrated smelters burn the plastics to refuel the machine and save money on power supply, but the treatment causes dioxin formation and therefore harms the environment. These facilities utilize either a molten bath or combustion to decompose plastic waste. For example, Umicore's smelters located at a refinery in Hoboken, Belgium has an annual capacity of 250,000 tons of material, and produces anywhere from 50 to 2400 tons of precious metals, Ag, Au, and Pt. Boliden Rönnskär smelter located in northern Sweden and the smelter by Noranda in Quebec, Canada, produce similar figures of precious metal extraction.

The above mentioned recycling facilities generalizes how plastics in WEEE are handled at an industrial level [11]. Research is being conducted to find new recycling methods that can reduce harmful emissions to the environment while preserving the plastic materials for reuse.

One method of preserving the plastic WEEE materials is through the thermal process called pyrolysis. It involves thermal decomposition of the materials without air, thereby reducing dioxin formation. Depending on the temperature used will yield either a liquid (oil) or gas substance [6]. At the industrial level, it reduces landfill space compared to other methods and allows facilities to save on resources [1]. The resulting oil from high temperatures of pyrolysis are contaminated with halogenated compounds such as bromine and chlorine. This is a direct result of the flame retardants in the plastics. A treatment to remove the compounds is necessary, and is what prompts this study.

1.4 This study

The main goal of this study was to identify the effectiveness of a pretreatment on plastic fractions of e-waste by observing its BFR content via pyrolysis. The pretreatment used on the fractions is soxhlet extraction (SE), and the solvents used are isopropanol and toluene. The fractions studied were PCBs, modem and WiFi plastics, and a general fraction of brominated plastics.

Soxhlet extraction is considered very inefficient at an industrial level due to time and resources, but remains a fundamental method to testing the extraction of persistent organic pollutants (POPs) such as polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs). Other methods (with improved efficiency compared to SE) which have been used in studies to extract flame retardants (out of organic samples such as soil for example) include accelerated soxhlet extraction (ASE), microwave soxhlet extraction (MSE), and soxtex extraction, to name a few. For example, ASE and solvothermal procedure allow for the desired compounds to be extracted above the solvent's boiling point, saving time on evaporating and cooling to begin extraction as with SE [13, 7].

Though these methods are regarded as being more efficient than SE, in previous studies it has been used as a reference for measuring the compound yield [12, 13, 14]. On an analytical scale, SE has yielded promising results, and was therefore a good starting point in this study to ensure extraction of flame retardants prior to starting pyrolysis.

2.0 Materials

2.1 Chemicals

Acetone, methanol, isopropanol, and toluene were the wet chemicals used for cleaning equipment (acetone), solvents for SE (isopropanol and toluene), and for concentrated extract samples (methanol). These chemicals were at 99.9% purity. The thimbles used for the SE apparatus were high purity glass microfiber thimbles (300mm x 100mm) purchased from GE Healthcare Life Sciences. Sodium hydroxide and hydrochloric acid were the dry chemicals used to prepare the bath for the SE apparatus to be sterilized.

2.2 Samples and Preparation for Soxhlet Extraction

Plastic fractions were obtained from a nearby waste facility in Sweden. The samples were prepared by blending large particles ($\approx 0.5\text{cm}^2$), followed by sieving the material on four trays for 15 minutes. The final particle sizes used for experiments were less than 0.09mm.

2.3 GC-MS Liquid Sample Preparation

After each iteration of SE, a sample of the extract was taken with the solvent remaining in the apparatus (diluted sample). After this sample was taken, the solvent was evaporated from the distillation flask either at room temperature or by using an oil bath. 4 mL of methanol were added to the dried extract in the distillation flask, then stirred until dissolved to obtain a concentrated sample. All of these samples went through the liquid autosampler for the GC-MS.

For soxhlet extraction of PCBs and modem and WiFi plastics using toluene, the dried extract would not dissolve in the methanol. A sample was taken, but another sample was gathered by dissolving a fixed amount of dried sample in toluene. This concentrated sample was used as a concentrated sample.

2.4 Pyrola Sample Preparation

After each iteration of SE, the original sample in the thimble was dried. For soxhlet extraction of PCBs and modem and WiFi plastics using toluene, the original sample was hardened inside the thimble. It was dried and crushed using a mortar and pestle.

3.0 Equipment and Methods

3.1 Soxhlet Apparatus

Prior to starting soxhlet extraction (SE), the apparatus was soaked in sodium hydroxide overnight. It was then washed with cleaning soap, tap water, and deionized water. The apparatus was dried using acetone, and placed in an oven at 105 °C. In between extractions, the apparatus was washed and soaked overnight in a beaker of hydrochloric acid, then washed and dried again.

Approximately 1g of the plastics were placed in the thimble in the apparatus. Extraction ran for 6 hours with an oil bath on a hot plate for constant heat. SE was completed for the three fractions twice - once with 100 mL of isopropanol, and again with 100 mL of toluene. For isopropanol, the distillation flask maintained a constant temperature of about 132°C, and for toluene, approximately 153°C.

3.2 GC-MS

For all samples, analysis was conducted using gas chromatography with a mass spectrometer (GC-MS), Agilent 7890A. The liquid auto sampler used is an Agilent 7693A. For the GC, the column used is an HP-5MS, fused with phenyl methyl silox (30m, 250µm film thickness, x 0.25mm inner diameter) containing (5%-phenyl)-methylpolysiloxane.

The injection of sample to the GC column was done in split mode, with the inlet heated to 280°C, and flow settings as follows: total flow at 24.7 mL/min, septum purge flow at 3mL/min, and split flow at 21mL/min. The split ratio was set to 30:1.

3.2.1 Liquid Samples

For analyzing the extract samples, the oven program was as follows: 125 °C for 1 min then 10 °C/min to 325 °C for 5 min.

3.2.2 Dry Samples (from Pyrola)

For dry samples, the oven program started at 40°C for two minutes. Then the temperature was ramped at a rate of 2°C/min to 140°C, then at 5°C/min to 240°C, and finally increased at 10°C/min to 315°C, held for 20 minutes. The total run time was 99.5 minutes.

3.3 Pyrolysis

Pyrola 2000 was used for analytical pyrolysis of the dry plastic fractions, connected to the GC.

4.0 Results and Discussion

4.1 Dry and Liquid Samples

Percent reductions in BFR content were calculated based on differences in average area per mass sample based on the chromatograms from the GC-MS. Multiple iterations of pyrolysis were run for each sample to better identify outlying data and the average abundance content. The liquid samples were analyzed for TBBPA only and the data gathered was only from one run.

4.2 Brominated Plastics

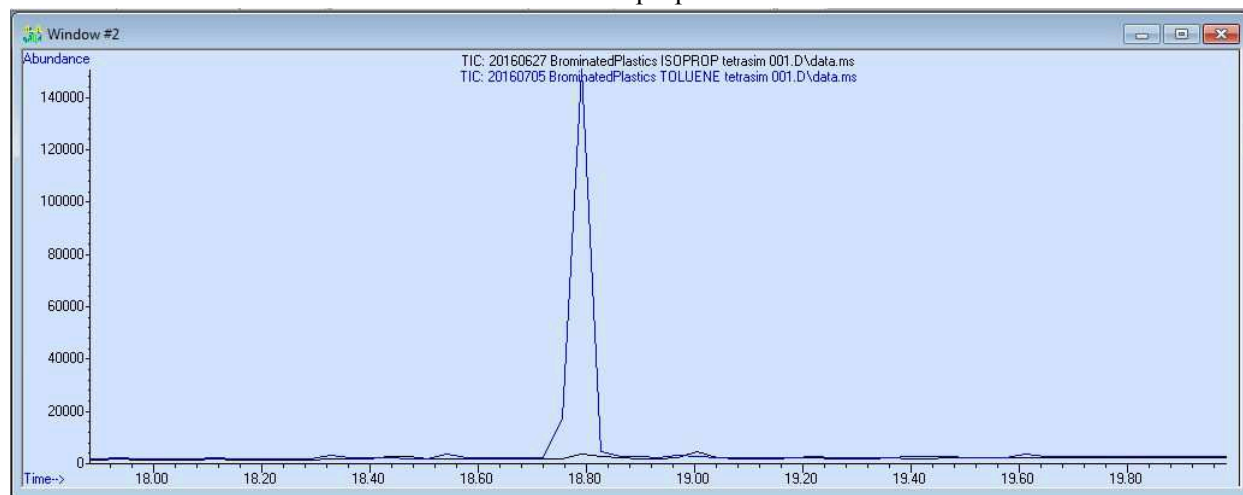
Three brominated compounds were detected across all runs for the untreated and treated brominated plastics samples: a polybrominated phenol compound (2,4,6 tribromo phenol), 2,5-dibromobenzo(b)thiophene, and tetrabromobisphenol A (TBBPA). The below data shows the percent

change in abundance of these compounds per mass of each respective sample. All brominated compound abundances found across all three samples of brominated plastics were successfully reduced via SE using toluene. Isopropanol had inconclusive results for tetrabromobisphenol A, but proved to be promising in abundance reduction for 2,4,6 tribromophenol and 2,5-dibromobenzo(b)thiophene.

Table 4.2.1 Percent reduction of brominated compounds compared to untreated sample content. Multiple iterations were carried out where needed to confirm trends in results.

Compounds	Brominated Plastics	
	Isopropanol treated	Toluene treated
TBBPA	-46.90%	$82.0\% \leq x$
2,4,6 tribromophenol	$89.58\% \leq x$	below detection limit
2,5-Dibromobenzo(b)thiophene	below detection limit	below detection limit

The liquid extract taken from soxhlet extraction were also run in the GC-MS, and were compared with the results of the dry sample analysis to see if any correlations were present. From the chromatogram, it is clear that toluene extracted more TBBPA than did isopropanol.



4.3 Modem & WiFi Plastics

Similar compounds were extracted across all samples of modem and WiFi plastics. Abundances of BFRs in these samples were varying compared to brominated plastics. Toluene treated plastics still had considerably lower abundances of TBBPA compared to isopropanol treated plastics. Generally speaking, abundances in the other three compounds identified were similar in reductions across both samples, with the isopropanol treated plastics typically having slightly higher abundance reduction on average.

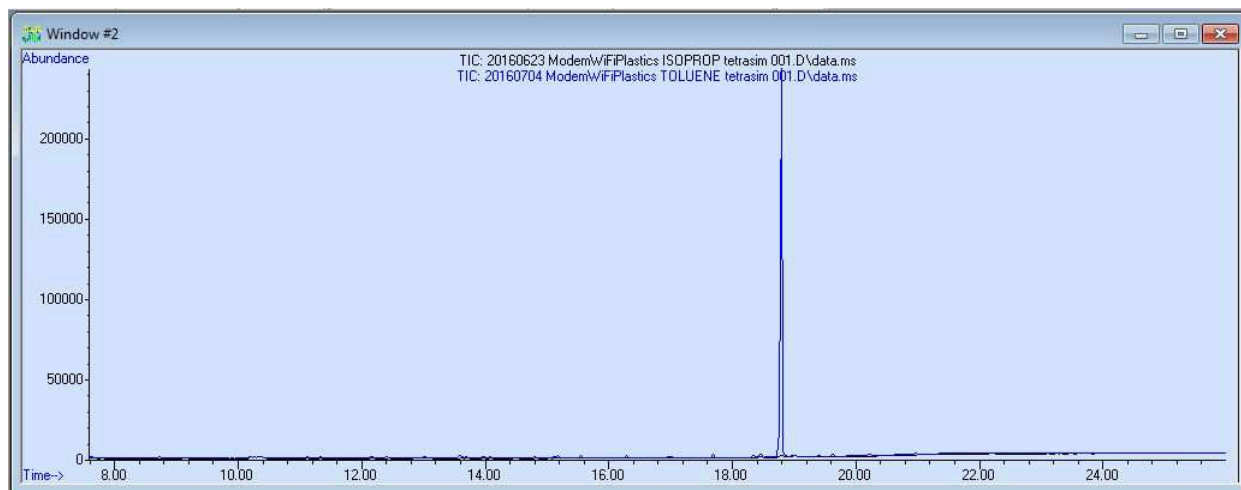
The average abundance per mass sample and the standard deviation of the data set for abundances of TBBPA in the isopropanol treated samples is 11,246.20 and 14,226.76, respectively. This standard deviation is very high and indicates a wide spread in the data. Though this reduction seems more promising than the abundance reduction in brominated plastics, it should be taken with caution since the

standard deviation is significantly high. Similar averages and standard deviations were calculated for toluene treated as well.

Table 4.3.1 Percent reduction of brominated compounds compared to untreated sample content. Multiple iterations were carried out where needed to confirm trends in results.

Compounds	Modem & WiFi Plastics	
	Isopropanol treated	Toluene treated
TBBPA	34.26%	81.63%
2,4,6 tribromophenol	90.44%	61.76%
Phenol 2,4-dibromo-	95.30%	90.46%
3,5-Dibromobenzo(b)thiophene	83.65%	71.64%

The liquid chromatogram revealed similar trends in TBBPA reduction for both samples as it did for brominated plastics. The reduction in TBBPA for the dried isopropanol treated plastics is more believable than for brominated plastics.



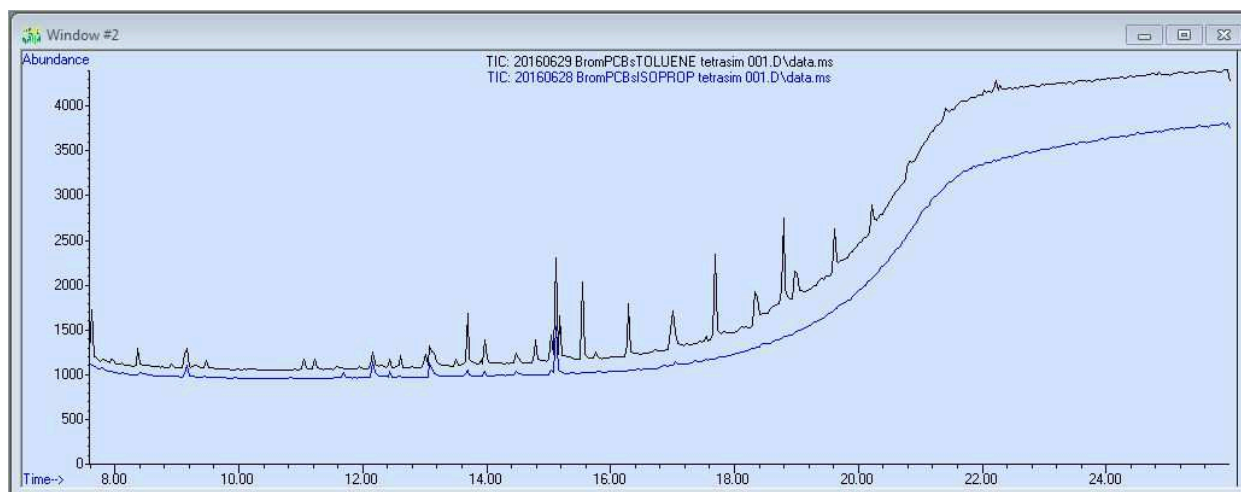
4.4 PCBs

For brominated PCBs, both samples of plastic waste had significant reductions in abundances of TBBPA. Isopropanol treated plastics showed better abundance reduction on average for 2,4-dibromophenol, while toluene treated plastics showed better reductions for bicyclo[4.2.0]octa-1,3,5-triene, 7,8-dibromo.

Table 4.3.1 Percent reduction of brominated compounds compared to untreated sample content. Multiple iterations were carried out where needed to confirm trends in results.

Compounds	Printed Circuit Boards	
	Isopropanol treated	Toluene treated
TBBPA	96.37%	96.59%
Phenol 2,4-dibromo-	55.81%	32.75%
Bicyclo[4.2.0]octa-1,3,5-triene, 7,8-dibromo-	44.98%	65.38%

The liquid extract chromatogram was inconclusive. For toluene treated PCB plastics, multiple peaks were identified as TBBPA, while isopropanol revealed a peak of its own. Based on the retention time in this study of the compound from brominated and modem and WiFi plastics, TBBPA should appear on the chromatogram between the 18th and 19th minute of the run. This was not the case for isopropanol treated PCBs, and for toluene treated PCBs, all of the peaks observed below were identified as TBBPA.



5.0 Conclusion

5.1 Experimental and Data Errors

The GC-MS experienced a physical malfunction in the inlet injector when processing the plastic fraction to the MS. Residue of the plastic samples remained in the inlet and therefore may have tampered with the results of these runs. It was first noticed that there was a problem when treated samples (isopropanol) of brominated plastics showed higher concentrations of TBBPA than untreated samples (-46% was the percent change calculated, indicating an increase in BFR content). These results indicate that a repeated study would be beneficial to confirm or challenge what was found in this study.

The standard deviation of the data varied greatly and indicated that the spread of the data gathered were too much to indicate repeatable results. For abundance reductions reported as being below detection limit, it is believed those are accurate since there was no average to calculate.

Almost no blanks were run in between each iteration of all of the samples until TBBPA levels appeared to be unusually high in an analysis of the dried samples that ultimately wasn't used. Running a blank in between each iteration going forward would've helped to detect a malfunction in the machine or in the method used, and could have yielded more accurate results but would have taken more time.

5.2 Conclusions

For brominated plastics, toluene was successful at reducing abundance levels of TBBPA. The liquid analysis of the extracted compounds furthers this conclusion since the abundance of TBBPA was high. It could be said that isopropanol was not a good solvent for extracting TBBPA based on the liquid sample chromatogram, but further analysis of the dried samples would need to be carried out to better make the claim. For modem and WiFi plastics, toluene significantly reduced TBBPA levels as well. The data gathered showed a wide spread, and should be completed again with the same method to either confirm or challenge what was found in this study. The plastics from PCBs showed similar results in toluene's effectiveness in extracting TBBPA compared to previous samples run, but the data gathered of the liquid extract tells a different story. The filament on the Pyrola damaged more quickly for this fraction than it did for brominated plastics and modem and WiFi plastics, which could have contributed to the varying results. The damage done to the platinum filament changes the resistance of the pyrola over time and ultimately leads to a need for recalibration.

Though the data has a wide spread and more experiments would help to confirm the results found in this study, toluene's aromaticity makes it a good solvent for extracting TBBPA, and other BFR's with a benzene ring. This contributes to further confirming that the results gathered are coherent to the extent of toluene's abilities as a solvent. Isopropanol is not aromatic, and this could explain its lack of inclination to extracting high levels of toluene (except in the case of PCBs).

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