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Evaluation of Antimony content in WEEE plastics and in PET

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SUMMARY

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ABSTRACT

This thesis has the aim of evaluating antimony content in plastic waste, especially in waste electric and electronic equipment (WEEE) and PET. Evaluating antimony content in plastic waste and the consequent possibility of its recovery is a topic of great interest, mainly for the following reasons:

- Because antimony is a raw critical material, whose 87% global production happens in China. EU is completely dependent on antimony importation and according to European Commission antimony will arrive to the highest “supply and demand deficit” in 2015-2020;
- Because antimony is present inside waste cycle, particularly within plastic waste;
- Because antimony could be a problem for human health. Antimony is classified by IARC (International Agency for Research on Cancer) as a possible carcinogenic substance (group 2B).

In the first part of the thesis a general picture on antimony is presented, with the primary purpose of explaining the reasons that make its recovery important. The main uses of antimony have been considered, especially in plastics, also mentioning the potential dangers for human health of exposure to antimony and its compounds. Then the methods developed for samples preparation and extraction experiments with acid solvents were described. The samples analyzed were plastic components from WEEE (ABS-HF-380) from a PC screen, mixed plastics from six mobile phones, PPE/PS+PC/ABS from a TV screen and PC/ABS from two laptops). Ashes were prepared from WEEE samples and analyzed. The analysis of the ash allowed to evaluate the potentially recoverable antimony from bottom ashes deriving from Municipal Solid Waste incineration, as some antimony-containing waste ends up with energy recovery. The sample with the highest antimony content derived from laptops: 765 mg/kg in plastic and 5766 mg/kg in ashes. Lower concentrations were detected in mobile phones: 3.2 mg/kg in plastic and 103.6 mg/kg in ash. PC and TV screen plastics showed antimony only in the ashes (829.34 mg/kg in PC screen, 1593.7 mg/kg in TV screen).

Furthermore, different types of PET were also analyzed: virgin PET, washed and shredded PET, PET derived from water and soda bottles. We chosed these specific PET samples to represent the different phases of the production cycle, recycling and reuse of the material. For virgin PET the average antimony content was 171.11 mg/kg. For the other PET samples, the average antimony contents were very close to those of the highest quality PET, with higher standard deviations due to the heterogeneity of the samples.

The use of different acid solvents (aqua regia, hydrochloric and sulfuric acids) has been assessed to evaluate their extraction efficiency on the considered plastic samples. In particular, hot hydrochloric

acid highlighted the possibility of recovering antimony from plastics without their complete destruction. In fact, positive results have been obtained for TV and PC screen plastics digested with hydrocholoric acid in microwave. Concentrated sulfuric acid gave positive results for all samples, proving to be an effective solvent for extraction, but it caused an almost complete distruction of the samples.

The experimental activity of this thesis was performed at Technical University of Hamburg Harburg (TUHH), Germany, under the co-supervision of prof Kerstin Kuchta, during a 6 months-stay funded by Politecnico di Torino. Data analysis and discussion of results has been carried out at DIATI.

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1.Introduction

The aim of this thesis is to develop an analytical procedure for the detection of antimony in plastics from WEEE and in PET bottles, considering the different fates of waste plastics. Evaluating antimony content in waste and the consequent possibility of its recovery is a topic of great interest for the research work, mainly for these reasons:

- Because antimony is a raw critical material, which 87% of global production is in China. EU is completely dependent on antimony importation and according to European Commission antimony will arrive to the highest "supply and demand deficit" in 2015-2020 (Dupont, Arnout, Jones, & Binnemans, 2016);
- Because antimony is present inside waste cycle
- Because antimony could be a problem for human health. Antimony toxicity was verified (especially for the skin and the respiratory tract) and it is classified by IARC (International Agency for Research on Cancer) as a possible carcinogenic substance (group 2B).

In the waste cycle, there are different possible destinations for plastic products. The analyses carried out in this thesis are based on waste plastics final treatments. They could be:

- Burned after being mixed with other urban waste or directly as secondary solid fuel
- Recycled, especially in the case of PET bottles

Secondary recovery of antimony is possible in polymeric matrices. The samples choice was made considering that antimony has two main uses in the production of polymers. Antimony is added, usually in the form of antimony trioxide, with halogenated flame-retardants (especially brominates). In this case, antimony is used as a synergistic additive to improve the effect of halogenated compounds. Significant antimony concentrations can be also found in PET, because it is one of the most widely used catalysts for PET solid condensation.

Based on all these reasons, acid digestion tests to assess antimony recovery from different plastic waste were performed. The key points on which the analyses were based could be listed as follows:

- Composition of the acid solvent used (aqua regia, hydrochloric and sulfuric acids)
- Temperature and pressure of the reaction
- Quantitative analysis, common for all tests, using ICP (inductive coupled plasma) – OES.

2.The importance of Antimony

Antimony (Sb) is a chemical element, to be precise a metalloid. Its atomic number is 51 and normally in nature it is found as stibnite (Sb_2S_3). This chemical element, with a gray colour, is really important especially for its use in plastics. Since Sb is present in many plastic materials, and for this reason it is found within the cycle of wastes. The word Antimony derives from greek language, precisely from the words *anti* and *monos* which means ´a metal not found alone´ (Anderson, 2012). In fact, antimony is a mineral resource that can be identified within different types of deposits. The first use of antimony was done by the ancient Egyptians, who used stibnite as a cosmetic (Anderson, 2012). The first industrial uses of antimony date back to the beginning of 1900, to form lead alloys for weapons munitions (Anderson, 2012). With the advent of technological innovations, antimony found many uses, especially to form lead alloys in lead-acid batteries and as flame-retardant.

2.1 Antimony: a raw critical material

EU countries haven’t within their territories a wide range of basic raw materials for the main industrial applications. These material, better known as “raw critical materials” (CRMs), are crucial for economy and EU is completely dependent on imports from non-European countries. For these reasons the European Commission identified the CRMs for EU countries, publishing a first list with 14 CRMs in 2010. With 2017 update the list reached 27 elements. CRMs were choosen evaluating the materials according to the methodology set out in the guidelines, drawn up by European Commission, and based on two indicators, “the economic importance” and the “supply risk” (European Commission & Directorate-General Joint Research Centre,2017). Antimony was included in the list since 2010, occupying a position of strong interest in the world economy. In fig.1, there are all the material investigated by European Commission. The materials represented with red dots are those that were classified as CRMs, while those represented in blue are the materials which resulted not critical. The two indicators considered the economic importance of the material for EU economy and the conditions of primary suppliers (actually available quantities and geopolitical situations) (Blengini, et al., 2017). In the specific case of antimony, in 2014 the European Commission estimated that the highest “supply-gap demand” would be reached in the 2015-2020 (Dupont, Arnout, Jones, & Binnemans, 2016).

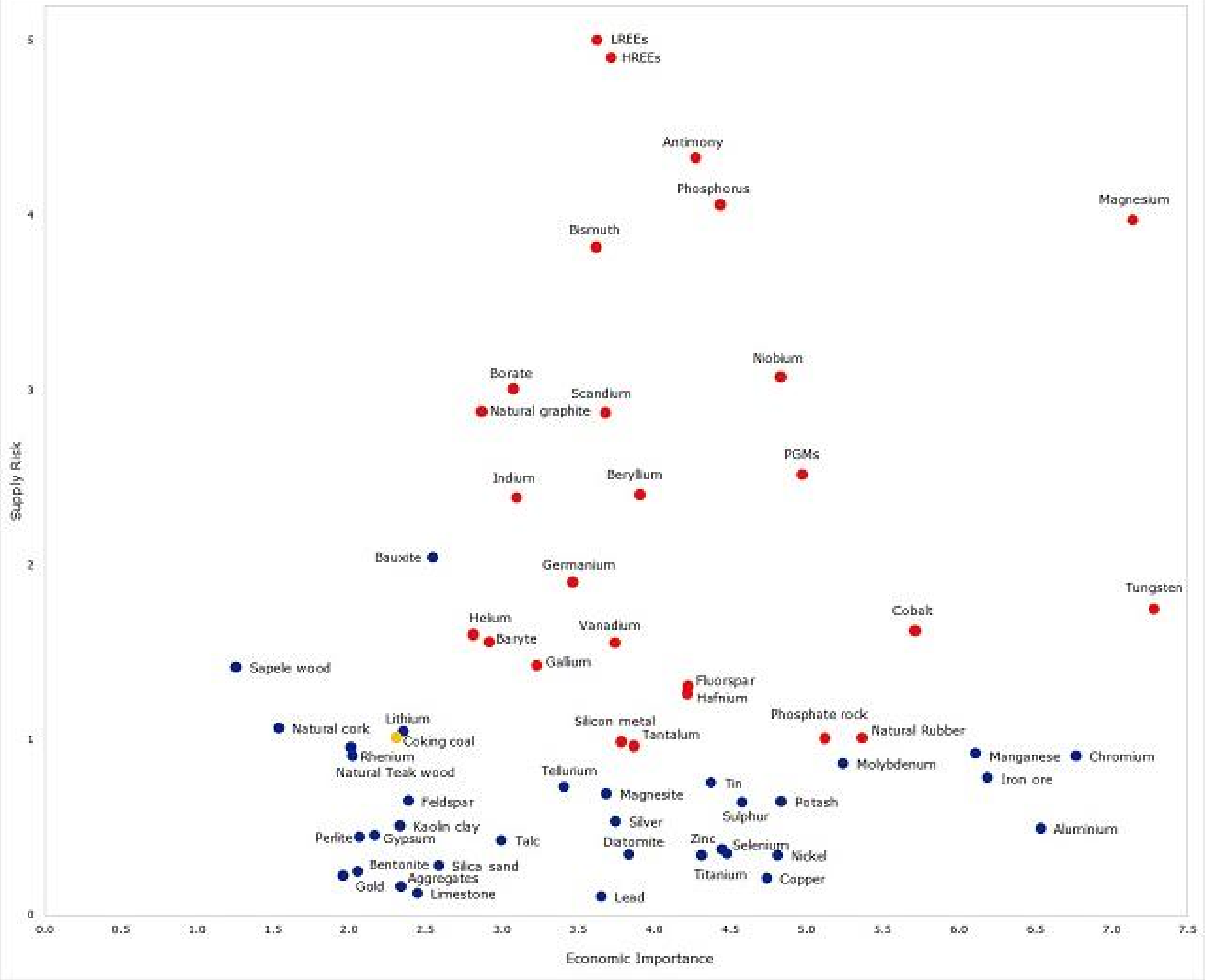


Figure 1 Results of the CMRs analysis, updated to 2017

(European Commission, European Commission: Growth, Internal Market, Industry, Entrepreneurship and SMEs, 2018)

2.2 Antimony: primary production and market

The undisputed leader of world antimony production is China, which holds about 87% of global supply (Ad hoc Working Group on defining CRMs, 2014). In tab.1 there are the most recent data on antimony mining production and reserves, collected and summarized by USGS (U.S. Department of the Interior & U.S. Geological Survey, 2018). It is clear why China occupies the role of absolute leader of antimony production. Among the mining forms of the antimony the most important, at an industrial level, is stibnite (Sb_2S_3), which is often present within quartz veins (Anderson, 2012). Stibnite is one of the typical mineral forms in which antimony occurs and from it antimony is obtained in metallic form or as antimony trioxide (Sb_2O_3).

Table 1 Mine production of antimony in 2016-2017 and Reserves

(U.S. Department of the Interior & U.S. Geological Survey, 2018)

	Mine production		Reserves
	2016	**2017**	
United States	-	-	60000
Australia	5000	5000	140000
Bolivia	2670	2600	310000
Burma	3000	2000	NA
China	108000	110000	480000
Guatemala	25	25	NA
Iran	200	200	NA
Kazakhstan	573	570	NA
Laos	242	240	NA
Mexico	196	200	18000
Pakistan	114	100	NA
Russia (recoverable)	8000	8000	350000
South Africa	1200	1200	27000
Tajikistan	14000	14000	50000
Turkey	4000	3500	100000
Vietnam	643	600	NA
World Total (rounded)	**148000**	**150000**	**1500000**

After undergoing mining processes, antimony ores can be treated with two types of metallurgical methods, to obtain antimony Sb metal or antimony trioxide (Anderson, 2012):

- "*pyrometallurgical methods*, which are based on the use of very high temperatures to allow Sb sulfides oxidation in Sb_2O_3 and the Sb_2O_3 reduction in metal form (*Oxide volatilization, Liquation, Oxide reduction, Iron precipitation, Blast furnace smelting*)"
- "*hydrometallurgical methods,* which are composed of two phases, i.e. a leaching process with an aggressive solvent and an elettrodeposition"

In fig.2 an exhaustive scheme of the two methodologies is reported.

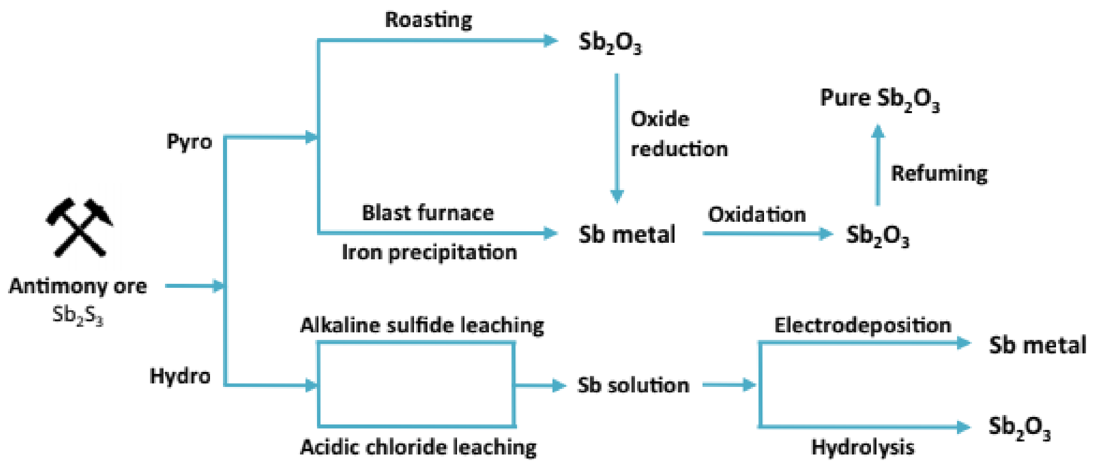


Figure 2 Flow sheet of metallurgical methods for antimony primary production

(Dupont, Arnout, Jones, & Binnemans, 2016)

Without going more into details of the extraction techniques used to extract the mineral antimony, it may be interesting to observe the antimony price trend of last years. In the last U.S. Global Resources (USGR) database update antimony prices per pound are reported. The antimony price decreased during the period between the end of 2014 and the beginning of 2016 ("from 4.05 to 2.6 $ per pound"), and in the following two years it had a rise ("around 4 $ per pound in 2017") (U.S. Department of the Interior & U.S. Geological Survey, 2018). To better understand the trend of antimony prices in the last ten years, in tab.2 average monthly prices are shown in $ per tonne. These data, collected and summarized by United States Antimony Corporation (United States Antimony Corporation-USAC , 2018), show the evolution of antimony market values. In fig.3 there is a grafic representation of antimony metal price from 2005 to the beginning of 2018, "based on the London Metal Exchange average price C.I.F. Rotterdam per metric ton" (United States Antimony Corporation-USAC , Antimony prices, 2018). Antimony market prices underwent significant fluctuactions, reaching the cheapest values in 2009 and 2016. In 2011 the most expensive was reached (around 17,879 $ per ton in april). In 2016, the main producers decided to reduce the antimony production due to lower prices and harsher government environmental directives (U.S. Department of the Interior & U.S. Geological Survey, 2018). These things, along with an increase in the export quota implemented by the "Chinese Ministry of Commerce" at the beginning of 2017 (U.S. Department of the Interior & U.S. Geological Survey, 2018), influenced antimony prices increase of the last two years.

Table 2 Average monthly antimony metal price per metric ton cif USA

(United States Antimony Corporation-USAC, 2018)

Month	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018
Jan	5952	4989	6583	14,027	11,85	11,492	9,877	8,543	5,456	7,683	8,609
Feb	6228	4839	6661	14,95	11,96	10,803	10,072	7,937	5,374	7,65	8,688
Mar	6027	4630	6697	16,452	13,051	10,626	10,141	8,234	5,511	8,653	
Apr	6002	4484	8488	17,879	13,503	10,458	9,866	8,488	5,585	8,945	
Mag	6404	4643	9287	16,769	13,917	10,351	9,711	8,616	6,283	8,763	
Giu	6663	5038	8860	15,997	13,977	10,183	9,755	8,3	6,504	8,548	
Lug	6561	5421	9425	14,815	13,531	9,893	9,797	7,824	6,724	7,937	
Ago	6746	6065	10,114	14,991	12,886	10,086	9,755	7,33	7,176	8,351	
Set	6724	6067	11,161	15,454	12,814	10,417	9,659	6,79	7,634	8,460	
Ott	6645	6471	11,343	15,419	12,911	10,472	9,469	6,462	7,785	8,157	
Nov	6393	6504	12,098	14,509	12,732	10,34	9,281	6,049	7,584	8,226	
Dic	5806	6355	13,228	13,062	12,125	9,893	9,039	5,677	7,606	8,510	
High	6746	6504	13,228	17,879	13,977	11,492	10,141	8,616	7,785	8,945	8,688
Low	5806	4484	6583	13,062	11,85	9,893	9,039	5,677	5,374	7,650	8,609
Avg	**6346**	**5459**	**9495**	**15,36**	**12,938**	**10,418**	**9,702**	**7,521**	**6,602**	**8,324**	**8,649**

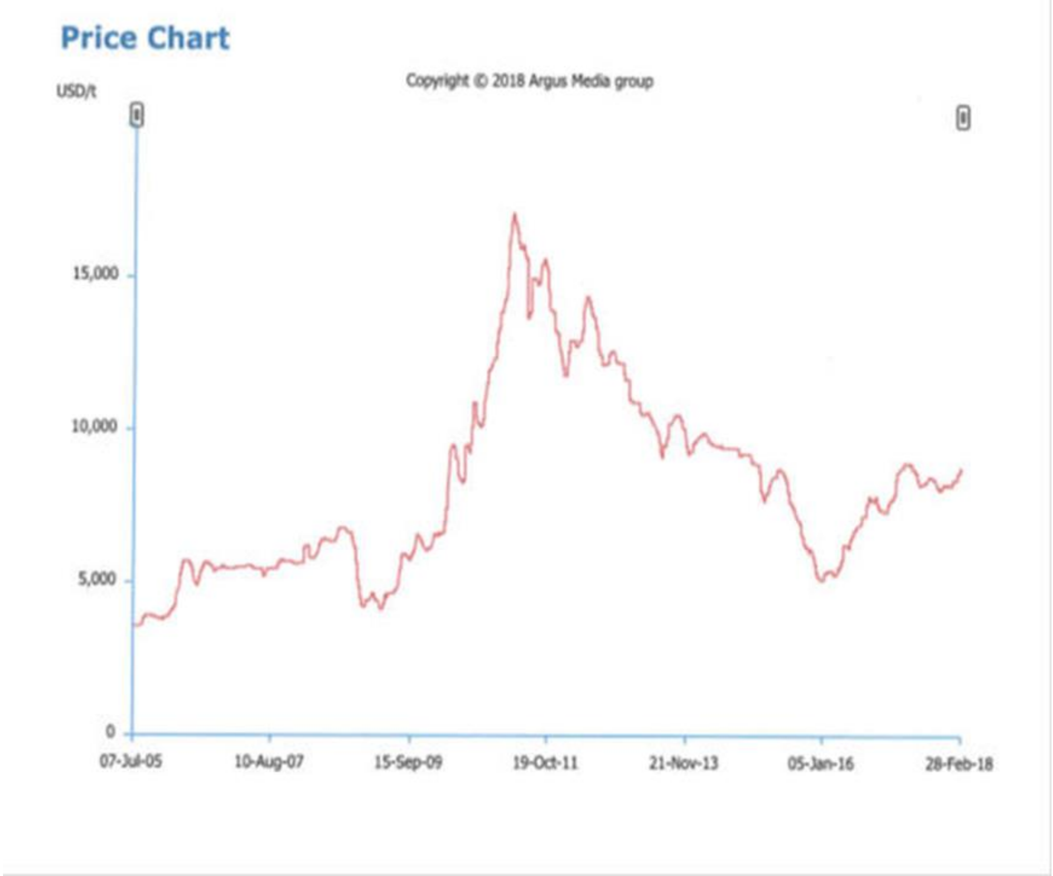


Figure 3 Antimony metal price trend,"based on the London Metal Exchange average price C.I.F. Rotterdam per metric ton"

(United States Antimony Corporation-USAC , 2018)

2.3 Flame retardants

2.3.1 The poor thermal resistance of polymers

Antimony (especially as antimony trioxide) is added in the matrices of polymeric materials as additive for flame-retardants. Flame-retardants are necessary to improve the thermal properties of plastics, because polymeric materials haven't good resistance against heat. Polymeric materials are generally appreciated for their "chemical resistance" (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). Polymeric structures are easily destroyed by combustion processes due to the hydrocarbon nature. In fact, the task of flame retardants is to reduce the vulnerability caused by the organic nature of polymers. Furthermore, for electrical products it is necessary to use plastic coatings with a certain resistance against heat and flames. The combustion of plastic material takes place quite easily. As all combustion processes, there is a need for a source of heat and a combustion agent, such as oxygen. The combustion process is endothermic: when a polymeric material is near a heat source, it begins to store energy. Heat absorption and the consequent development of combustion depend on the characteristics of the polymer, in particular from the following characteristics (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009):

A) “heat-storage capacity”
B) “enthalpy of fusion”
C) “degree of crystallinity”.

It is clear that polymeric decomposition’s dynamics occur according to the type of polymer involved, trough the combined action of heat and oxygen: it is possible to divide decomposition processes in two types, i.e. “non-oxidizing thermal degradation and oxidizing thermal degradation” (Pal & Macskasy, 1991). The “oxidizing thermal degradation” involves oxygen in the air, while the non-oxidizing process is triggered by a pyrolysis reaction.

2.3.2 Flame-retardants action

Flame-retardants are a wide range of substances, which are added to plastics, because they are able to increase the resistance of polymers against the development of thermal degradation processes. In this section the main flame-retardant characteristics will be explained, without describing in detail all flame-retardant types. There are two main mechanisms by whom flame-retardants act:

- physical action
- chemical actions.

Some flame-retardant additives are able to inhibit the combustion trigger using physical mechanisms. When the degradation process is starting, they could dilute the fuel or create a “superficial protective layers” (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). The fuel dilution is possible because these additives release inert gases, as vapor, which mix with combustible gases (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). An additional effect of some additives consists in being able to create a “protective solid or gaseous layer” which is able to put itself in the middle, from solid phase where there is the polymer degradation to gaseous phase where there is the development of combustion, managing to hinder the development of reactions (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009).

For what concerns the chemical action (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009), there are some flame-retardants, which intervene directly by modifying the combustion reactions in the gaseous or solid phase. It is possible to distinguish, in the case of the chemical mechanism, the following phenomena (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009):

1) “The formation of halogenated free radicals which inhibit the development of free combustion radicals in gas phase”;

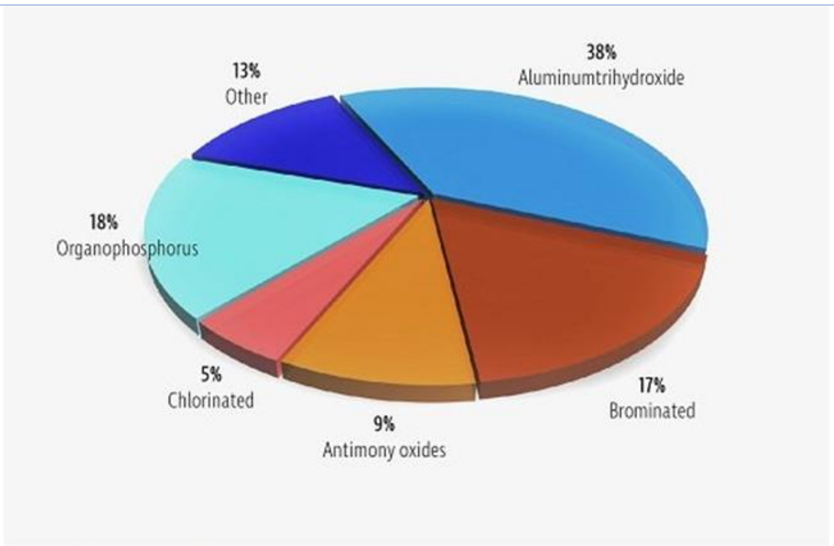
2) “The formation of a carbon or glassy layer that arises between the gas and condense phases”;
3) “The acceleration of polymers splitting from the bulk of the plastic material, removing combustible material from the reaction zone”.

2.3.3 Flame-retardants use and antimony as flame-retardant

Flame-retardants role in polymer world is crucial, because they are able to increase polymers’ thermal resistance. This big range of substances is consumed in quantities that exceed “2.25 milion t/y” (Corp. Clariant, 2017). Although the substances could be used as flame-retardants are a lot, but 3 of them are mostly consumed. “IHS consulting 2017” reported the amount of flame-retardants percentage consumption in 2016 and the main countries consumed it (IHS Consulting, 2017). From fig.4, it could be possible to observe that the top 3 flame-retardants we could find in plastics are:

1) 38 % Aluminumtrihydroxide, $Al(OH)_3$;
2) 18 % Organophophorus compounds;
3) 17% Brominated compunds.

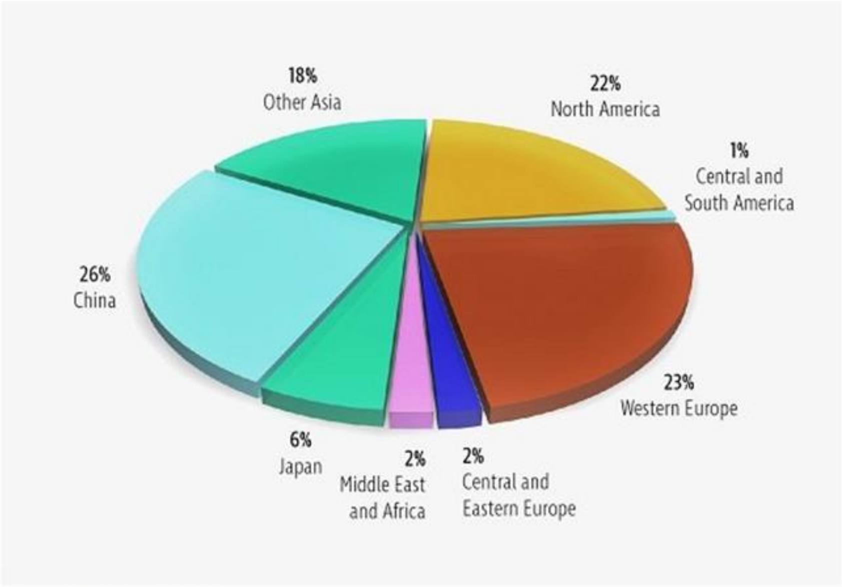
Antimony is shown to be the 4th most applied flame-retardant. Its application is directly related to the presence of the so-called ‘Halogenated flame-retardants’ (brominated and chlorinated substances).



Source: IHS Consulting 2017

Figure 4 Percentage of flame-retardants consumed in 2016

(IHS Consulting, 2017) (Corp. Clariant, 2017)



Source: IHS Consulting 2017

Figure 5 Percentage of flame-retardants consume pour Countries

(IHS Consulting, 2017) (Corp. Clariant, 2017)

For example, fluorine halogens don't thermally decompose in most polymers temperature range, while iodine compounds have less thermal resistance than polymers (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). Chlorine and bromine halogenated compounds are very common flame-retardants, because their thermal decomposition takes place in the same temperature range of most types polymers (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). The halogenated compounds release their corresponding halogenated acid during thermal decomposition. In the case of Chlorine and bromine compounds, they release HCl and HBr, which then react with combustion free radicals and as a result Cl* or Br* are formed, more stable and less reactive radicals.

In industrial practice different types of flame-retardant additives are incorporated into polymeric products, in order to be able to exploit the synergies of the different flame-retardant mechanisms. When the combustion process begins, it can be slowed down by the simultaneous action of the added flame-retardants. The combination of more flame-retardants inside a product, allows the exploitation of two different anti-combustion mechanisms, or the upgrade of a specific one. In the case of halogenated additives, their gas phase's action is increased thanks to the addition of antimony trioxide (Sb_2O_3) or zinc borate. Add antimony trioxide, in an amount corresponding to the

5-30% of the halogenated additive's weight (United States Antimony Corporation-USAC, 2017), enhance the effect of delaying flame. During the decomposition of halogenated flame-retardant additives, antimony trioxide (Sb_2O_3) reacts with the corresponding halogens acids (HCl or HBr) and as result antimony oxyhalides are formed (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). Antimony oxyhalides, like $SbCl_3$ and $SbBr_3$, are more persistent than the starting halogen acids and they react more with free combustion radicals, managing to remove them more effectively (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009). For example, the synergistic reaction between HCl and Sb_2O_3 creates a sequence of reactions that remove H* and regenerate continuously HCl:

$$"SbCl_3 + H * \rightarrow HCl + SbCl_2 *$$

$$SbCl_2 + H * \rightarrow HCl + SbCl *$$

$$SbCl + H * \rightarrow HCl + Sb *"$$

From the paper 'New prospects in flame retardant polymer material: From fundamentals to nanocomposites' (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, & Dubois, 2009)

Besides these reactions, antimony's radical and oxide could take part in parallel with other reactions and increase the removal of free combustion radicals (Lyons J. W., 1987):

$$"Sb * + OH * \rightarrow SbOH$$

$$SbOH * + H * \rightarrow SbO * + H_2$$

$$SbO * + H * \rightarrow SbOH"$$

Given its wide use as a synergistic flame-retardant additive, antimony is considered a CRMs also for its importance in the production of polymeric materials. To get an idea of the polymeric materials in which the use of brominated flame-retardants is required, and therefore also the presence of antimony trioxide. In tab.3 there are the the percentage of antimony trioxide added to halogenated flame-retardants additives (United States Antimony Corporation-USAC, 2017).

Table 3. percentage of antimony trioxide added to halogenated flame-retardants during plastic manufacture

(United States Antimony Corporation-USAC, 2017)

Plastic	**Fiammability**	**Antimony trioxide (wt%)**	**BFR required?**
PE	High	from 8 to 16	Yes
PP	High	from 5 to 15	Yes

PS	High	10	Yes
PU	High	10	Yes
SBR	High	from 5 to 30	Yes
ABS	High	From 5 to 12	Yes
PVC	Low	From 1 to 10	No

2.4 Antimony as catalyst in PET production

Antimony, in the form of Sb_2O_3, is used as catalyst in the production of poly(ethylene terephtalate), more commonly known as PET. PET production process involves one of the following reactions as first step:

1) esterification between terephtalic acid (TPA) and ethylene glycol, with water formation (the process takes place in a range of temperature between 230-250 °C, with a pressure of 3 atm);
2) transesterification between ethylene glycol (EG) and dimethyl terephthalate (DMT), with methanol formation.

The common result of these two reactions is the formation of PET monomer, called "bis(2-hydroxyethyl) terephthalate (BHET)". Transesterification process was very used in the past because the market didn't offer terephthalic acid with sufficient degree of purity. Furthermore, it wasn't possible to control the heterogeneous esterification process due to the insolubility of TPA in ethylene glycol (Soccio, 2008). Today esterification is the most exploited, thanks to the presence on the market of high purity TPA, and for the optimization of the esterification process (Soccio, 2008). The passage from the use of the transesterification process to that of esterification is important, as it concerns the consumption of catalysts. For example Kokkolas et al. (Kokkolas, Bikiaris, & Karayannidis, 1998) studied that an antimony trioxide concentration until 1000 ppm increases lineary the rate constant of transesterification process, while they also showed that esterification process takes place independently of Sb_2O_3. It could be assumed that in the past the use of antimony for PET production was higher, because antimony trioxide influence in the case of transesterification (today it is prefered the esterification that doesn't require Sb_2O_3).

The next step is the polymeritazion reaction, also known as polycondensation reaction of monomers. In this phase of process, the use of a catalyst is necessary, so as to allow the growth of the polymer. According to Duh, the use of a catalyst, especially antimony trioxide, helps the development of "very high molecular weight (i.e.>24000) PET" (Duh, 2002). Antimony trioxide is one of the most appreciated catalysts in PET polycondensation, mainly for the following reasons (Duh,2002):

- it offers a high catalytic activity, even if not the best;
- its use does not cause the formation of undesired colors in the final product;
- among all the available catalysts, it tends to favor very little the development of unwanted secondary reactions.

For Shash et. al (Shah, Bhatty, & Gamlen, 1984) antimony is the most appropriate catalyst for BHET polycondensation process compared to all the other elements investigated, i.e. “Pb,Ti,Mn,Sn and Zn”. They came to this conclusion because they found that antimony is among all the catalysts that develops degradation reactions more slowly, in addition to being the third more reactive into catalyst process, behind only to Ti and Sn. Having an appropriately catalysed solid-state polycondensation (SSP) is important because it is necessary to limit the lowering of polymer molecular weights, which occur especially in melting phase.

In industrial practice, polycondensation takes place at temperatures between 250-290 °C and under vacuum (0,1 mbar) (Soccio, 2008). Before adding the catalyst, Sb_2O_3 is transformed in antimony glycolate. In particular Sb_2O_3 reacts with ethylene glycol (EG), because it is dissolved inside EG at a temperature around 150 °C with the support of a nitrogen cover (Duh, 2002).

Duh (United States of America Patent n. 4,205,157, 1980), as it is possible read inside US Patent 4,205,157, patented a method for production of high molecular PET. He said that it is necessary an antimony concentration around 100 ppm, in order to obtain the maximum solid-state polymerization (SSP) rate for a polymer with “0,25 dl/g IV” (when the carboxyl content is near 0). In 2002 Duh (Duh,2002) found in his research that maximum SSP rate was obtained with an antimony concentration around 150 ppm. He justified the lower antimony concentration value inside US Patent 4,205,157 claiming that probably the prepolymer used had a particle size too big for a reaction-controlled SSP. In the literature it is full of examples of production processes for the manufacture of PET. In fact both in the production of virgin PET, and in production starting from a percentage of recycled, there are different patterns and different possibilities. For the production of virgin PET, when antimony is used as a catalyst, indications of antimony used concentrations could be found between 100 and 500 ppm. TH. Rieckmann (Rieckmann, 2003) describes the main physical conditions that are necessary to implement a typical polycondensation in batch plant, where 200 ppm of Sb_2O_3 are normally used (“T max=285 °C and P=1 mm Hg”).

2.4.1 Antimony inside PET production from recycled plastic

In these last years the world has known an increase in PET production. The recycling techniques evolved and their application is increasingly necessary, above all because of the increasing production of plastic products (especially PET). In literature there are lots of information regarding PET recycling techniques. However, the purpose of this paragraph is not to talk in detail about the recycling of PET, but we want to try to highlight how antimony intervenes in recycling processes. The reuse of PET to produce new plastic bottles requires that it be added to virgin PET. In fig.6 it is showed a flow sheet of PET reuse (Culbert & Christel, 2003).

In the flow sheet the two main methods of PET recycling are highlighted (Culbert & Christel, 2003). In the “Mechanical bottle-to-bottle recycling” the recycled PET is added to virgin PET after SSP step, in form of irregular pellets. In this chase the antimony is added only in virgin PET. The “Chemical recycling” involves the depolymerization of recycled PET and its subsequent polymerization together with virgin PET. There are two other flow sheets (fig 7, fig 8), for the main steps of the production of virgin PET and for its recycling in case of partial depolymerization (Welle, 2011).

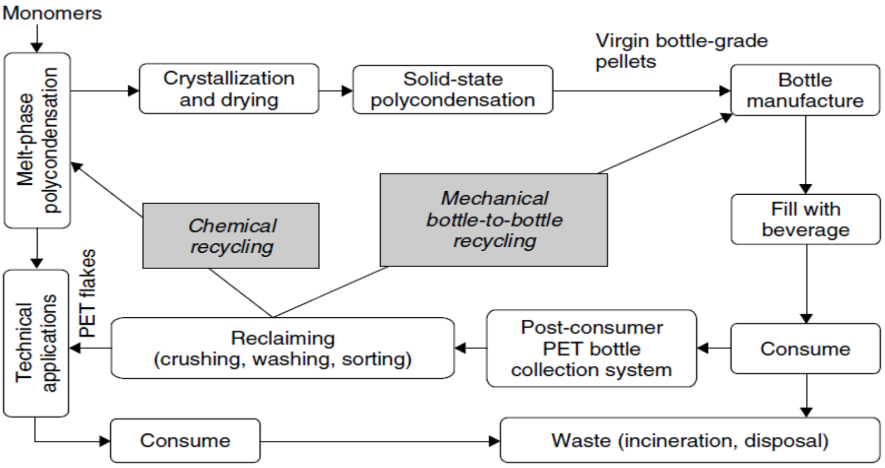


Figure 6 typical flow sheet of PET

From “Continuous Solid-State Polycondensation of Polyesters”

(Culbert & Christel, 2003))

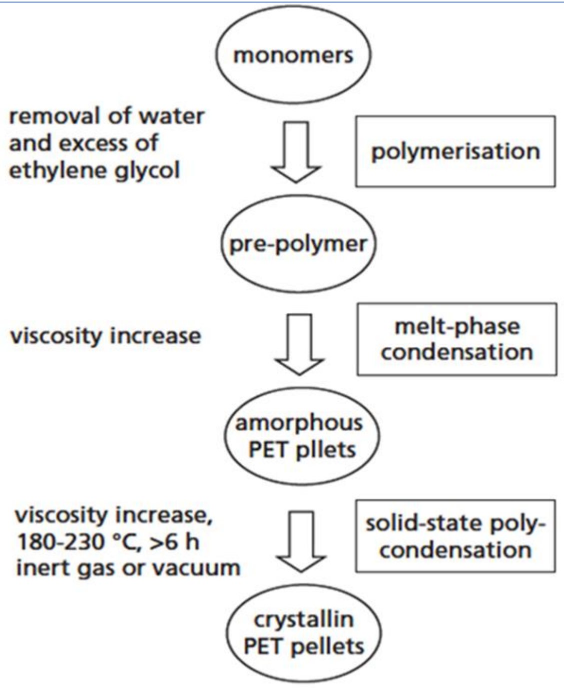


Figure 7 Main steps of virgin PET production

Image from the paper “Twenty years of PET bottle to bottle recycling-An overview” (Welle, 2011)

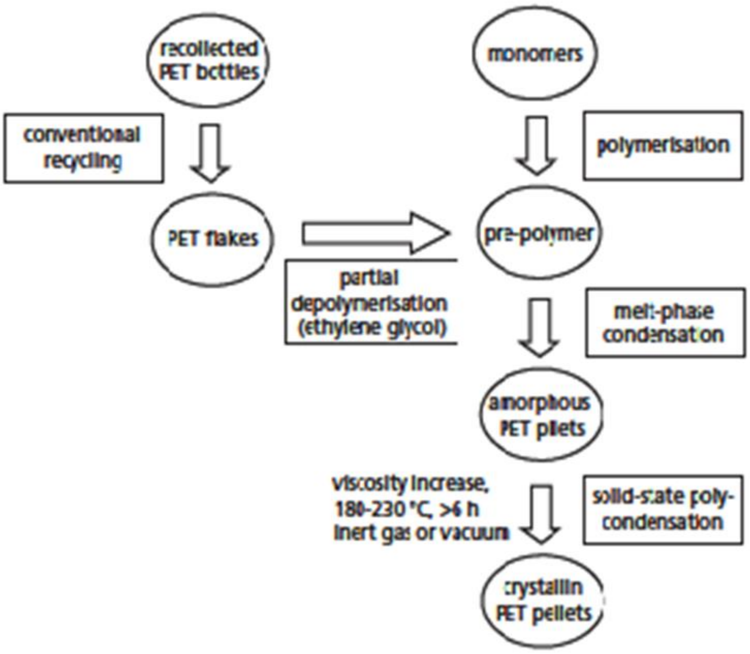


Figure 8 The main steps of “PET super-clean recycling processes based on partial depolymerisation

Image from the paper “Twenty years of PET bottle to bottle recycling-An overview” (Welle, 2011)

In both processes catalysts, especially antimony, play a fundamental role in the success of the final product. For what concerns the production of virgin PET, antimony could be added in pre-polymer phase (before the melting) and it will work to speed up the SSP. It is the same in PET production with recycled material, i.e. there is a polymerization phase followed by melt-phase condensation and especially solid-state polycondensation too. If the monomers are formed with a transesterification process, antimony trioxide could be introduced in polymerization step, adding it mixed with EG. PET is a material that can be recovered with different recycling techniques. The recovered PET, for example after conventional recycling, could be mixed with virgin material and they could became new crystalline PET pellets after a solid-state polycondensation. In the SSP antimony plays its role as a catalyst. On the one hand it is used for virgin PET polycondensation, on the other we could find antimony trioxide or antimony glycolates inside the recycled material. They are present in their active forms (Duh, 2002) and, thanks to this thing, polyester polymer chains could be reassemble in longer crystallin PET chains (Welle, 2011). One of the main problems in PET recycling is that polymers decrease their molecular mass, because of the degradation processes that take place during original use and after recovering processes and for the depolymerization process. SSP is a really important step and thanks to it PET polymers could arrive to an higher molecular mass.

2.5 Antimony’s recovery from wastes

One of the most important challenges in the coming years is the refinement of the waste cycle. The production of waste is constantly increasing, together with the reduction of the availability of many raw materials. Among the hottest topics on which the European community is paying attention, there is the implementation of circulary economy efficiency. In January 2018, European Commission published a report concerning CRMs and their role in circular economy. In this report a focus was placed on the potential recovery of CRMs from wastes, underlining the importance of developing better recovery processes. In fig.9 there are the CRMs “End-of-life recycling input rate” (EOL-RIR), i.e. the percentage of material from secondary sources that satisfies the demand, elaborated by JRC and “based on the 2017 CRM study and on the MSA study 2015” (European Commission, 2018). In the current scenario, antimony is one of CRMs with the highest percentage of reuse. The 28 % of EOL-RIR derives monstly from the recovery of lead-acid batteries (European Commission, 2018), because in addition to the plastics antimony has been widely used in alloys with lead. The classic lead-acid batteries contain lead grids or plates, to which the mechanical resistance can be increased thanks to the addition of small percentages of antimony. Today this type of batteries has been replaced by other technologies, but their wide use in the past makes them an important component in the waste cycle.

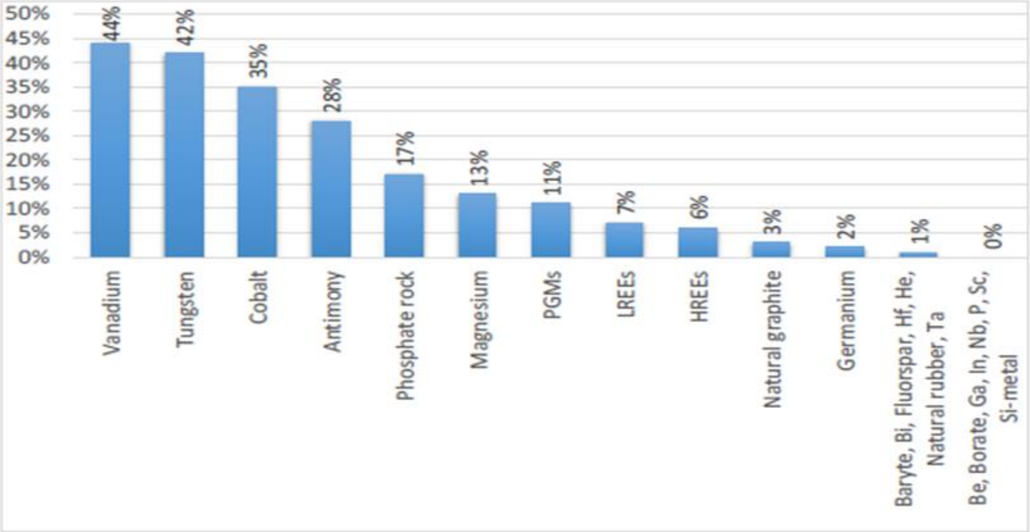
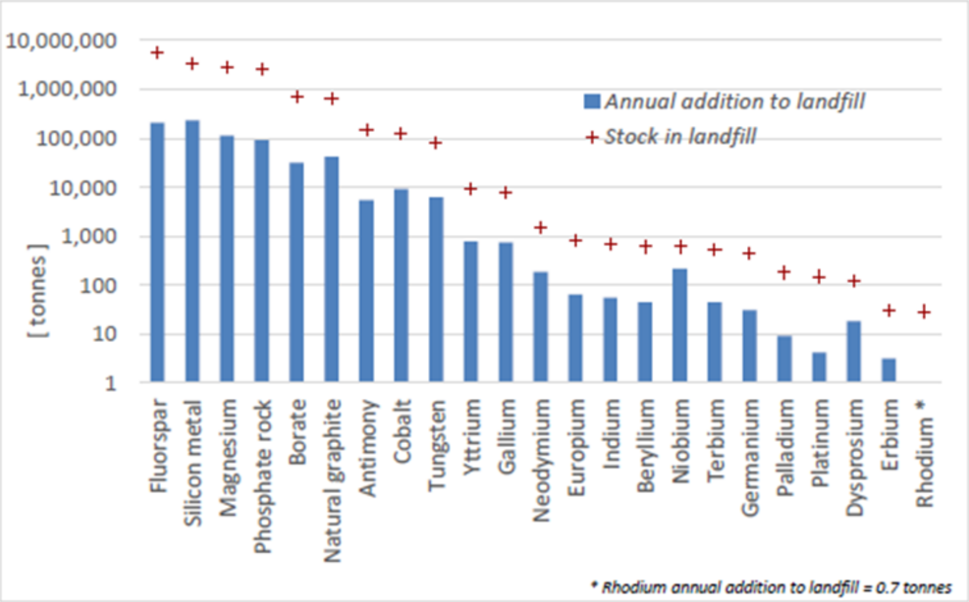


Figure 9“End-of-life recycling input rate by JRC elaboration, based on the 2017 CRM study and 2015 MSA study”

(European Commission, 2018)

From the available data the possibilities of antimony recovering from the waste seem satisfactory, even if not completely exploited. Significant amounts of antimony and other CRMs are not properly recovered and, according to MSA study of 2015, almost 10,000 t/y of antimony is stocked in EU landfills (fig.10) (European Commission, 2018).



** Rhodium annual addition to landfill = 0.7 tonnes*

Figure 10 “CRMs in landfills,JRC elaboration of 2015 MSA study”

(European Commission, 2018)

Waste management in the European context is very heterogeneous and in many Countries it must be improved. One of the causes of antimony presence in landfills, and also in municipal solid waste incineration (MSWI) ashes, is the incorrect management of waste electric and electronic waste (WEEE). In fact, the components of the electronic equipment are composed of potentially recoverable elements, including also antimony used mainly as flame-retardant. To get an idea of this, the tab.4 shows the average annual consumption of metals for components of electrical and electronic equipment (EEE) (Bueken & Yang, 2014).

Table 4 yearly demand of metal for EEE

(Bueken & Yang, 2014)

	Yearly demand for EEE (T/Y)	Percentage of total production (%)
Cu	4500000	30
Sn	90000	33
Sb	65000	50
Co	11000	19
Ag	6000	30
Bi	900	16
In	380	79
Au	300	12
Se	240	17

WEEE are a precious source of recoverable by-products. Plastic components of WEEE may have significant antimony content, potentially recoverable and reusable. Among the most used plastics in EEE there is ABS (Acrylonitrile-butadiene-styrene), where antimony trioxide is often added as flame-retardant. In tab.5 there are the percentage of more common polymer in some components of WEEE (Delgado, Barruetabeña, & Salas, 2007).

Table 5 Polymer composition of EEE

(Delgado, Barruetabeña, & Salas, 2007)

WEEE item	Polymer composition
Printers/faxes	PS (80%),HIPS (10%), SAN (5%), ABS, PP
Telecoms	ABS (80%), PC/ABS (13%), HIPS (5%), POM
TVs	PPE/PS (63%), PC/ABS (32%), PET (5%)
Toys	ABS (70%), HIPS (10%), PP (10%), PA (5%), PVC (5%)
Monitors	PC/ABS (90%), ABS (5%), HIPS (5%)
Computer	ABS (50%), PC/ABS (35%), HIPS (15%)
Small household appliances	PP (43%), PA (19%), ABS-SAN 17%), PC (10%), PBT, POM
Refrigeration	PS&EPS (31%), ABS (26%), PU (22%), UP (9%), PVC (6%)
Dishwashers	PP (69%), PS (8%), ABS (7%), PVC (5%)

2.6 Antimony environmental problems

A large amount of research world interested to antimony focused attention on its fate in the environment. Only in these last years there is more attention to antimony recovery possibilities, mainly due to the strong dependence of the EU on the Chinese market. Thus, the main target of this work is an assessment of antimony recovery possibilities, but it is important to create a good picture about its environmental problems too. Antimony is present in the environment in very low concentrations, as U.S. Department of Health and Human Service highlighted in their report called "Toxicological profile of Antimony" (Agency for Toxic Substances and Disease Registry , 2017). In this report it is written that antimony concentrations in air range between >1 ng/m^3 to 170 ng/m^3, while in soil normally they don't overpass 1 ppm. Furthermore, they reported that antimony concentrations in food could be between 0.2 to 1.1 ppb (Agency for Toxic Substances and Disease Registry , 2017). All toxicological and epidemilogy studies analyzed the effects on human health of exposure to antimony and its compounds. When we talk about the antimony compounds, we refer to (Agency for Toxic Substances and Disease Registry , 2017):

- "antimony organic forms ($C_8H_{10}K_2O_{15}Sb_2$, $K_2Sb_2(C_4H_2O_6)_2*3H_2O$, $C_6H_9O_6Sb$)"
- "antimony inorganic trivalent (Sb_2O_3, $SbCl_3$, Sb_2S_3, SbH_3)"
- "metal antimony"
- "antimony inorganic pentavalent (Sb_2O_5,Sb_2S_5)"
- "antimony-containing drugs"

2.6.1 Antimony as carcinogenic compound

Possible carcinogenic effects were observed within a "antimony smelter facility", because of an increase in lung cancer cases among workers (Schnorr, Steenland, & Thun, 1995). Older studies that dealt with the same theme for antimony workers could be find in "Survey of antimony workers: Mortality 1961-1992" (Jones, 1994). In literature there are a series of studies concerning the possible carcinogenic effects of Sb_2O_3, performed on rats (Agency for Toxic Substances and Disease Registry , 2017). Thanks to studies, IARC classified antimony trioxide as a possible carcinogenic substance, i.e. belonging to group 2B (salute, 2016). For the ingestion of antimony compounds instead there is not sufficient evidence, since the studies on the rats mentioned above report results only with regard to the respiratory tract. More recent studies investigated the possibility of carcinogenic effects due to antimony ingestion. In particular, there are two epidemiology studies focused on the risks related to the ingestion of water containing antimony compounds. Colak et al. conducted a study on Turkish citizens concerning the possible relationship between antimony levels (all < 20 μg/L) in water and cancer incidence, finding positive results (Colak, Yomralioglu, & Nisanci, 2015). Mendy et al. tried to find if there is a correlation between "antimony urinary content" and carcinogenic risk, without results (Mendy, Gasana, & Viera, 2012).

2.6.2 Antimony Toxicity

In this section some of the results from the toxicological studies on humans and animals are reported. All the results with scientific evidence regard the toxic properties of antimony and its possible interactions with the human body. The respiratory tract is one of the most sensitive traits when antimony is taken by inhalation. The most common and light effects are pneumoconiosis and the irritation of the respiratory tracts, as reported in several studies on “workers involved in the extraction of antimony trioxide from minerals” (Agency for Toxic Substances and Disease Registry , 2017). Animal studies showed that the severity of the effects of inhalation of antimony compounds depends on the concentrations and duration of exposure. Chronic and long-term exposure to antimony trioxide was studied by Newton et. al in rats, who observed a growth in the number of “alveolar and intra-alveolar macrophages” related to intermediate and long-term exposures (Newton, Bolte, Daly, & et. al, 1994).

Studies on the effects of antimony on health have also found significant results for the skin. Studies have shown that working exposures to antimony compounds may be related to the onset of dermatitis, as for example reported in the studies of Potkonjak & Pavlovich (Potkonjak & Pavlovich , 1983) and White et. al (White, Mathias , & Davin, 1993) in workers exposed to airbone antimony. They concluded that the exposure to airbone antimony is related to the formation of pustules and rashes and that the high temperatures favourite this type of dermal effect.

Other studies showed possible antimony cardiovascular and gastrointestinal effects (“vomit,ulcers, diarrhea” ecc..), without being able to derive certain correlations (Agency for Toxic Substances and Disease Registry , 2017). A possible source of antimony exposure that has been studied in recent years is water inside the PET plastic bottles. The antimony in PET of plastic bottles can leach into the water, especially when the bottles are heated. When the water bottles are left in the car's trunk in the summer with the heat of solar radiation, the antimony percolates in water in larger quantities. A study on this phenomenon was done by Westerhoff et. al, who studied the growth of antimony content in the bottles of water due to heating (Westerhoff, Prapaipong, Shock, & Hillaireau, 2008).

3 MATERIALS AND METHODS

3.1 Acqua regia extractions

3.1.1 Experimental plan aqua regia extractions

In this section materials and methods used for laboratory experiments will be described.

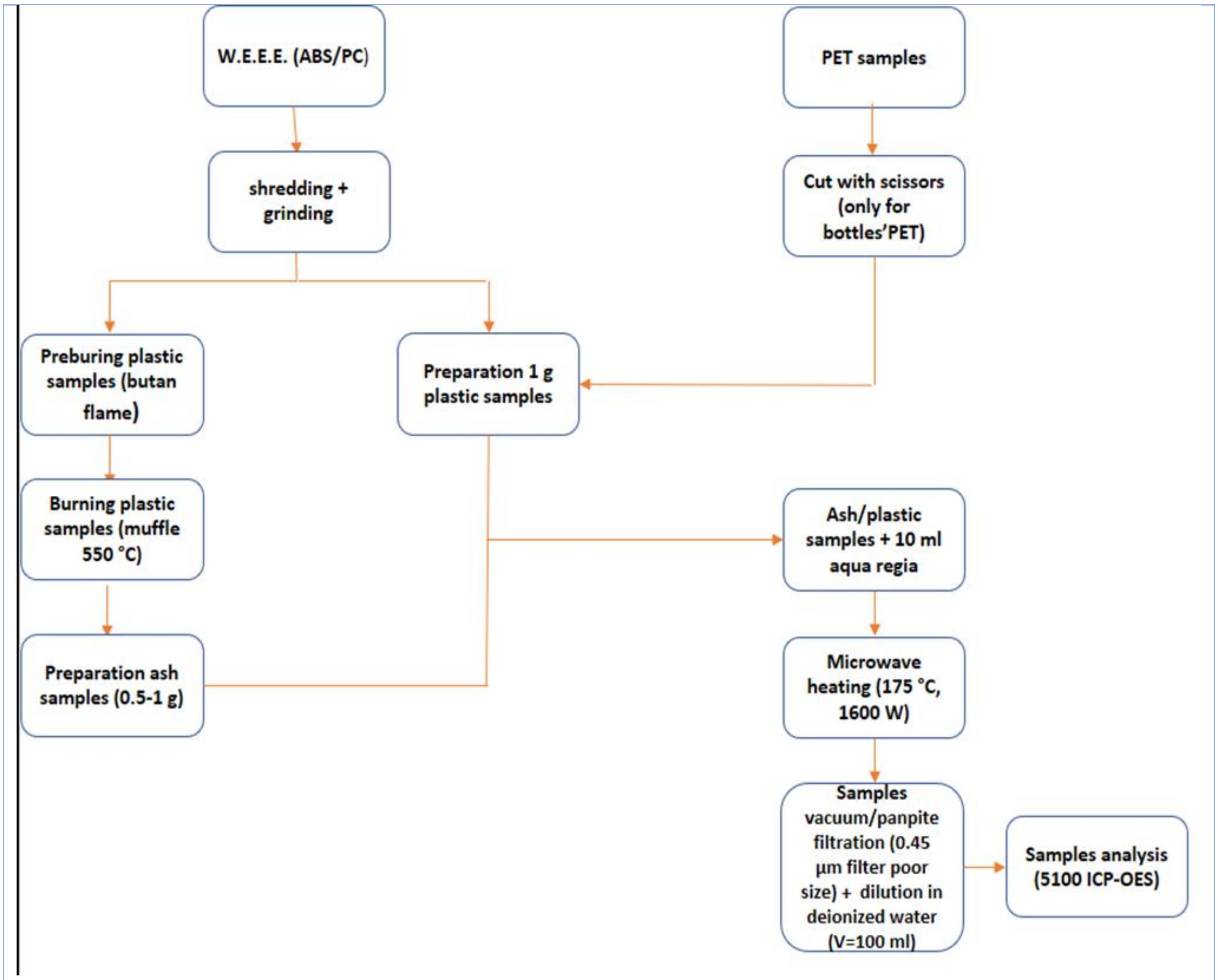


Figure 11 flow sheet about aqua regia experiments plan

The experimental plan, shown in fig.11, was performed using two types of samples:

- WEEE plastic samples
- PET samples

For WEEE plastic samples, ashes samples were also prepared. For ashes preparation, the procedure written inside standard DIN EN ISO 3451-1 was used. For all the samples, an acid digestion with aqua regia inside a microwave has been applied, following procedure B of DIN EN 16174-2012. After digestion in a microwave oven, the samples were diluted and filtered and finally analyzed with the ICP.

3.1.2 WEEE samples preparation

Based on availability at IUE, plastics derived from 4 different types of electronic equipments were sampled:

I. ABS-HF-380 from a PC monitor (LCD MONITOR ACER, model AL801);
II. PC/ABS from laptop's plastic (two models: an HP SERIES HSTNN-105C and a notebook XYRON);
III. ABS/PC from a mix of old generation mobile phones (plastic from 6 mobile phones);
IV. PPE/PS and PC/ABS from a TV screen (a GRUNDIG Amira 30 LW 76-9401 TOP).

Figure 12 mobile phones

Figure 13 PC screen

Figure 14 TV screen

Figure 15 Laptops

Once all non-plastic parts have been carefully removed, the plastic pieces were reduced into smaller pieces. The biggest pieces were cut with a saw and then they were reduced in a blade shredder

Figure 16 Blade shredder

Figure 17 Blade crusher

(fig.16). After the shredder, the size of WEEE plastic pieces was further lowered with a crusher (fig.17). Inside the crusher, under the blades, a screen with 4 mm meshes was placed. The rotation speed of the blades has been set at 7 rpm.

Thanks to the use of the crusher, plastic samples of a few millimeters were obtained (fig18-21).


Figure 18 shredded TV screen


Figure 19 shredded laptops

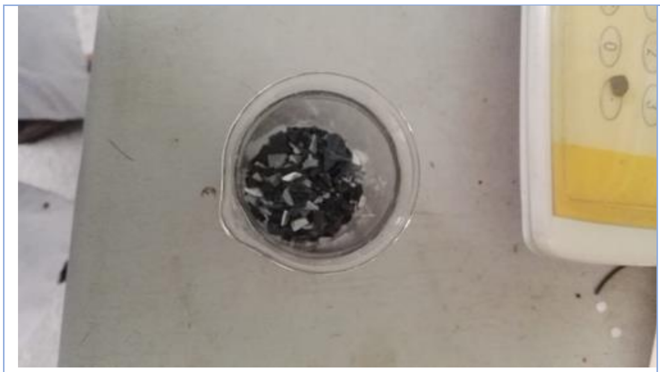


Figure 20 shredded mobile phones


Figure 21 shredded TV screen

3.1.3 Ash samples preparation

ISO 3451-1 is a standard that gives indications on how to prepare the ashes from the plastics. The standard proposes three different procedures for a correct preparation of the ashes. In the present thesis work the indications of procedure A were followed, which don’t require the use of sulfuric acid (procedures B and C provide for the use of sulfuric, so as to favor the removal of organic residues). First of all, the samples were placed inside porcelain crucibles. The crucibles were half filled with plastic and were pre-burned through a butane flame (fig.22). It is very important, before complete combustion, the use of a pre-burner for at least half an hour (depending on the specific sample). Pre-combustion is necessary to significantly reduce the organic quantity of the sample, so as to have carbonized samples easier to burn. Moreover, thanks to the pre-combustion, the bad smells that would derive from the direct burning of plastic in muffle were avoided. To obtain a sufficient quantity of ash, during the pre-combustion, plastic quantities were added when the volume of the sample in the crucible was reducing.

Figure 22 Butan flame

During preburning it is important to avoid the presence of living flames, because it increases the loss of fly ash. In fact, the pre-combustion process took place under the hood and each time a flame formed, it was stopped with a glass cup. Once the butane flame was heated, the samples were placed inside a dryer. In order to completely eliminate the organic fraction from the samples, they were burned 3 hours inside a muffle (600 °C). These 3 hours of burning were divided into 30 minutes intervals each. After 30 minutes of cooking, the samples were removed from the muffle and placed an hour inside the dryer. The drying of the samples is necessary to be able to weigh them and to have a measurement without the interference of humidity. It is important to note that the standard recommends not to exceed 3 hours of muffle burning. In case the ash sample reaches the mass constancy before 3 hours of muffle burning, it is possible stop earlier the heating process. In fig.23 there is a picture of the ash prepared with the procedure A.

Figure 23 Plastic ashes

Inside of ISO 3451-1 there is a recommendation regarding the amount of ash that needs to be obtained. The purpose of the tests is the correct implementation of the combustion process and, for a great evaluation of input plastic samples' inorganic content, the ashes weight obtained must be from 5 to 200 mg. In table. there are the average indications of the quantities of plastic to be burned, according to their inorganic content.

Table 6 from "DIN EN ISO 3451-1: Plastics- determination of ash-part 1:General methods"

(DIN EN ISO 3451-1: Plastics- determination of ash-part 1:General methods, 2008)**, sample quantity based on approximate ash content**

Approximate ash content (%)	Sample quantity (g)	Mass of the produced ash (mg)
≤ 0.01	≥ 200	About 5 to 10
> 0.01 to 0.05	100	10 to 50
> 0.05 to 0.1	50	25 to 50
> 0.1 to 0.2	25	25 to 50
> 0.2 to 1	10	20 to 100
> 1 bis 10	5	50 to 500
> 10	2	200

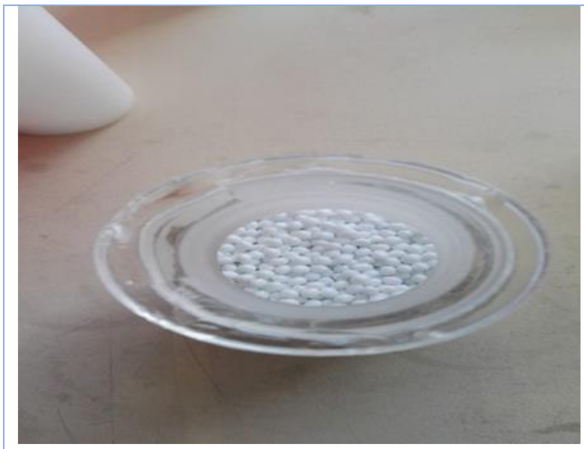
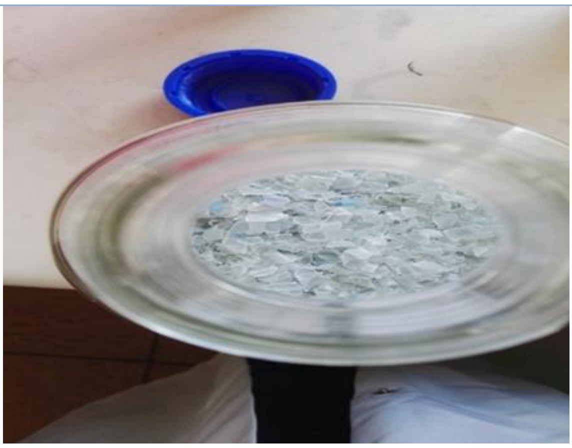
3.1.3 PET samples preparation

As for PET, the samples used are (fig.24-27):

I. virgin PET of new production;
II. washed and shredded PET coming from VEOLIA, ready to be treated and recycled;
III. PET from Coca cola bottles;
IV. PET from water bottles.

PET samples preparation was easier than others, because the only samples to chop were the bottles (it was enough the use of scissors). In fact, the PET from VEOLIA was already shredded and virgin PET was in the form of pellets.

 Figure 24 Water bottles	 Figure 25 Coca cola bottles

 Figure 26 Virgin PET	 Figure 27 Shredded and washed PET
Virgin PET	**Washed and shredded PET**

3.1.4 acid digestion with aqua regia + microwave heating

After preparing the samples, it was possible to proceed with the extraction process. EN ISO 16174-2012 describes two possible procedures for the aqua regia digestion (EN ISO 16174-Sludge,treated biowaste and soil-Digestion of aqua regia soluble fractions of elements, 2012):

1) “Method A: thermal heating under reflux conditions”
2) ”Method B: Microwave heating with temperature control at (175±5)°C”

It was decided to follow Method B. Furthermore the standard states that the procedures are suitable for the assessment of the presence of some specific chemical elements, antimony too. To apply acid digestion, the samples were weighted and placed inside microwave vessels (fig.28). Plastic samples of 1 g and ash samples of 0.5-1 g have been used. The procedure establishes the addition of aqua regia which is formed by reacting 3 moles of HCl with 1 mole of HNO_3. For each sample 10 ml of aqua regia were prepared using 7.5 ml of a solution 37% HCl and 2.5 ml of a solution 65% HNO_3.

Figure 28 Microwave vessels

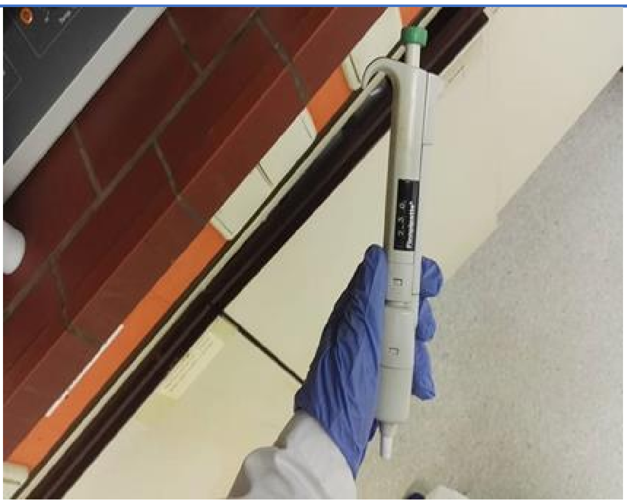


Figure 29 Electronic pipette

Aqua regia was prepared adding reagents directly into the microwave vessels with an electronic pipette (fig. 29). The vessels were closed with the appropriate containers and then they were heated inside a microwave, model MARS 6 (fig.30). Microwave heating was performed with the aim of speeding up the acid digestion of the samples and the program parameters used are shown in table 7.

Figure 30 Vessels inside microwaves

Figure 31 Closure of vessels

Table 7 Microwave heating program parameters used

•

Microwave heating program parameters	
Temperature	175 °C
Power	1600 W
Pressure	800 psi
Ramp Time	15 min
Hold Time	10 min

3.1.5 Sample dilution and filtration

To complete the extraction procedure, it was necessary to dilute the samples and filter them to eliminate any solid-phase components. Thus, each vessel was opened and deionized water was added. Meanwhile the samples were diluted, they were filtered up to have solutions of 100 ml volume each. All samples were filtered with 0.45 µm pore size filters, so as to have diluted solutions without particulates. The filtration process was carried out in two different ways:

1) Vacuum filtration: the samples were diluted and passed trough a paper filter with the help of a pump used to suck the air and speed up the passage through the filters (fig. 32).

Figure 32 Vacuum filtration

2) Filtration with a panpipe: in this type of filtration, a panpipe was used (fig.33-34). The diluted sample was taken with the panpipe and passed through appropriate filters.

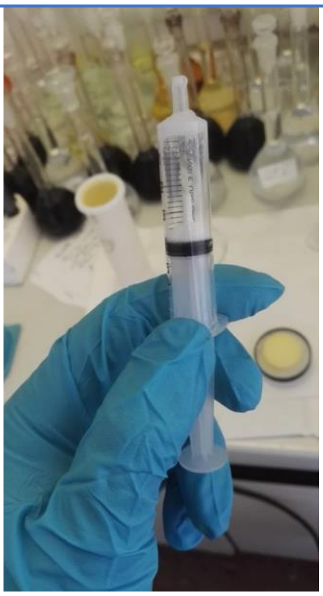


Figure 33 Panpite

Figure 34 Panpite filtration

Both filtration methods are valid. Usually the vacuum filtration is faster, but when the samples is too dense it could be necessary working with the panpite filtration.

3.1.6 ICP Analysis

The final step was the ICP Analysis. After all the digestion process, a series of liquid samples with dissolved trace elements were obtained. To analyze them, they were put into test tubes. Furthermore, for each sample, a 90 % diluted duplicate was prepared. To prepare the duplicates, one ml of each sample was mixed with 9 ml of deionized water. The machinery used for the test was an Agilent 5100 ICP OES (fig.34).

Figure 35 Agilent 5100 ICP OES

The analysis yielded results in ppm, i.e. mg/l considering the solution composed mostly of water. Remember that for all samples the dilution volumes ($V_{dilution}$) and the original weights (kg_{sample}) were measured. With all this data available, it was possible to calculate the Sb content of original samples. Below there are the calculations steps.

$$ppm = \frac{mg_{Sb}}{l_{solution}} \rightarrow mg_{Sb} = ppm * V_{dilution} \rightarrow Sb_{content} = \frac{mg_{Sb}}{Kg_{sample}}$$

To notice that Kg_{sample} could refer to plastic or ash, depending on the original sample. Having performed for each type of plastic sample test in triplicate (in duplicate for ashes samples), it was possible to calculate middle values with standard deviation. Furthermore, each result in ppm before being used was corrected with the results obtained from the blank samples.

3.2 Acid digestion with HCl and H_2SO_4

3.2.1 Hidrocloric acid digestions

Other acid solvents were tested only for WEEE plastics. Several tests were made with HCl, using it in different concentrations (6 M and 12 M). Tests were performed both with microwave heating and without. Below in fig.36 there is a flow sheet of the tests carried out with HCl.

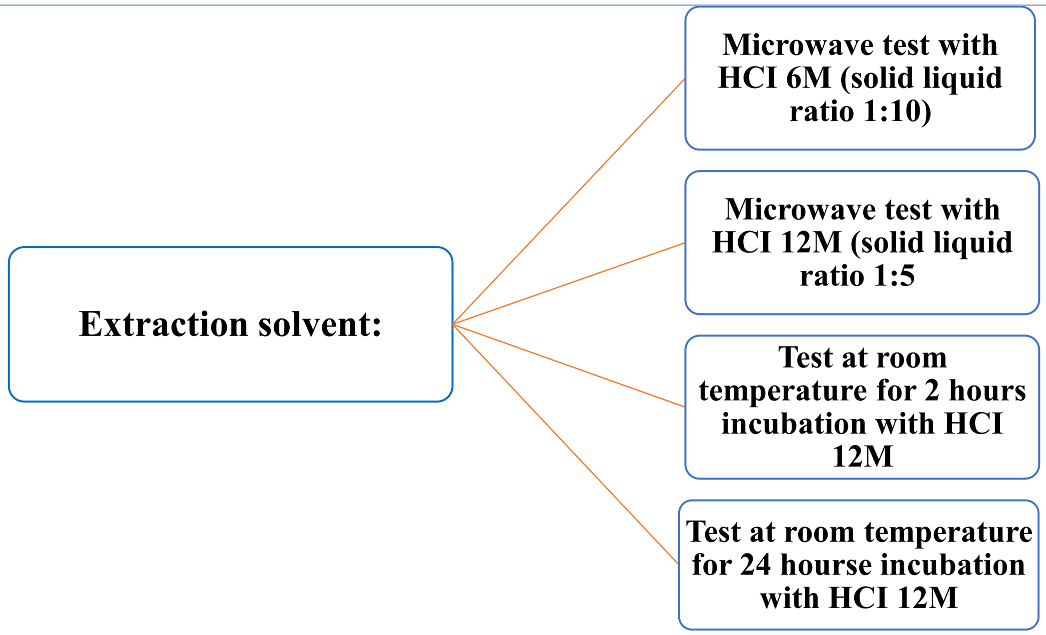


Figure 36 HCl experiments

The HCl solutions were prepared with the following formula, having all the data available from the labels of the solution 37% HCl ($\rho = 1.19\, {}^{kg}/_{l}, PM = 36.46\ g/mol$). Calling $M_{diluted}$ the molarity of the diluted HCl solution ($M_{diluted}$=6 M or 12 M), $M_{37\%}$ the molarity of 37% HCl solution and V_2 the total diluted volume that you want to get, it is calculated:

$$M_{37\%} = {}^{\rho}/_{PM} \rightarrow M_{37\%} * V_1 = M_{diluted} * V_2 \rightarrow V_2 = \frac{M_{37\%} * V_1}{M_{diluted}}$$

Therefore HCl diluted solutions were prepared by mixing V_2 of HCl 37% with (V_1-V_2) of deionized water. Tests with HCl 12 M were made using a solid liquid ratio L/S=5ml/g (2 g of plastic with 10 ml of HCl 12 M), while the test with HCl 6 M using a solid liquid ratio L/S=10 ml/g as aqua regia test. Tests with microwave heating found the same steps reported in EN ISO 16174-2012 and used for aqua regia extraction, with the only difference in the extraction solvent. As reported above, tests were also performed with 12 M HCl without using microwave heating. In this case, the samples were placed inside the jars and with the addition of HCl 12 M (fig.38).

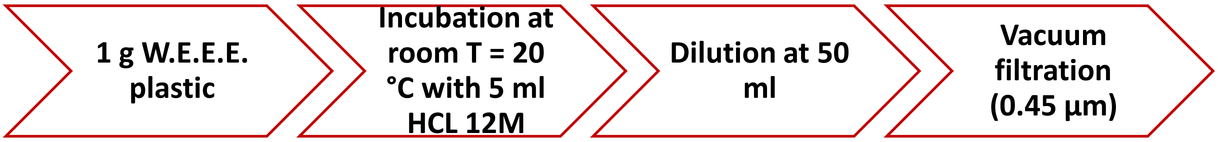


Figure 37 Room temperature tests flow sheet

Figure 38 Incubation of samples at room temperature

For heat-free tests, done in triplicate, two incubation times were chosen (2h and 24 h). The filtration and the content analysis were performed following the same procedure using for aqua regia extraction (fig.37).

3.2.2 Sulfuric acid extractions

Finally, an extraction was also tested with concentrated sulfuric acid. The same procedure is followed for all microwave tests, applying two filtrations instead of one (fig. 39). In fact, sulfuric acid is very aggressive towards organic compounds and in the test the samples were completly carbonized and dissolved in solution (fig.40). For this reason, two filtrations are necessary.

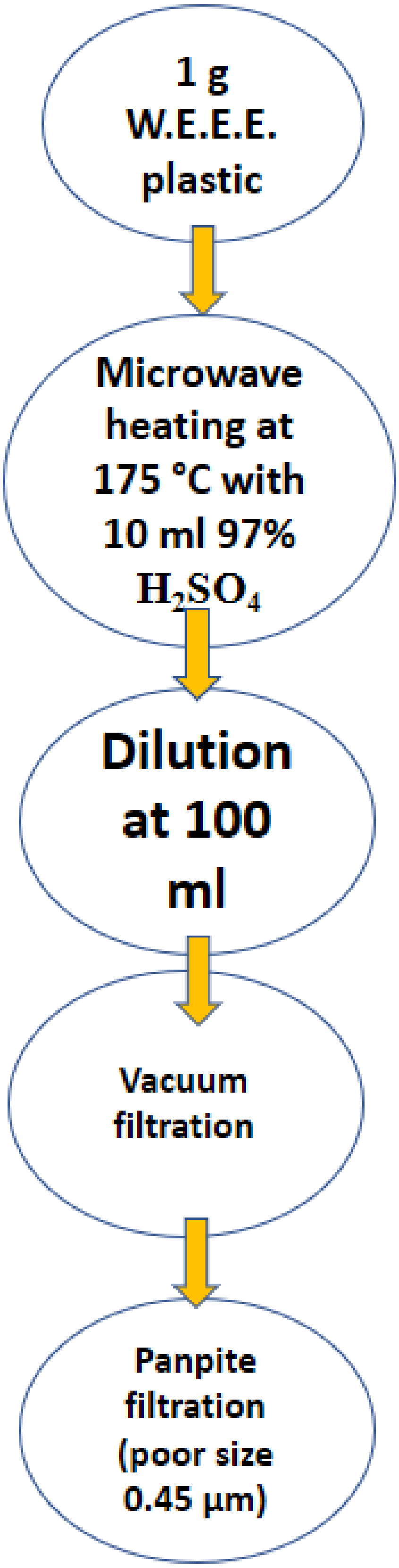


Figure 39 Flow sheet sulfuric acid extraction

Figure 40 Samples after sulfuric acid concentrated digestion

4.RESULTS AND DISCUSSION

4.1 Aqua regia extractions

4.1.1 Ash sample preparation

Before talking about the results of the analyzes carried out with the ICP, it will be discussed the determination of WEEE inorganic content. This analysis, performed preparing ashes, was applied only in WEEE plastics. For PET ashes weren't prepared, considering that their destiny in wastes cycle is monstly the reuse. For all the WEEE samples, it was performed 30 minutes of preburning. Only for laptop samples the preburning lasted 1.5 h because laptop samples were really hard to control. In fact, during preburning laptop plastics had an increase in volume, caused by a gas development (fig.41). It wasn't possible to burn a big amount of laptop plastic in crucibles and it was decided to proceed adding small quantities inside crucibles. From time to time, when the volume increase was shrinking, more laptop plastic was added. Thus proceeding, it was avoided to have samples leaking from the crucibles.

Figure 41 Laptop preburning, during the increase of volume

All plastic samples, for the evaluation of inorganic content, weighed around 5-6 g. With an effective preburning the samples lost around 2/3 of their original weight. During the 3 hours of burning at 600 °C, the samples weight decreased significantly because of the losing of organic content.

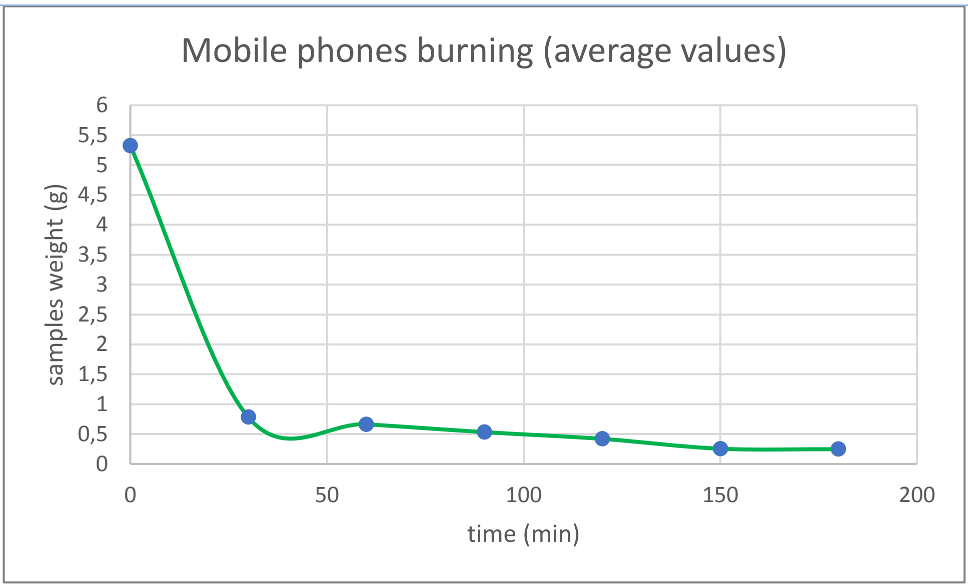


Figure 42 Burning mobile phones decreasing of weight

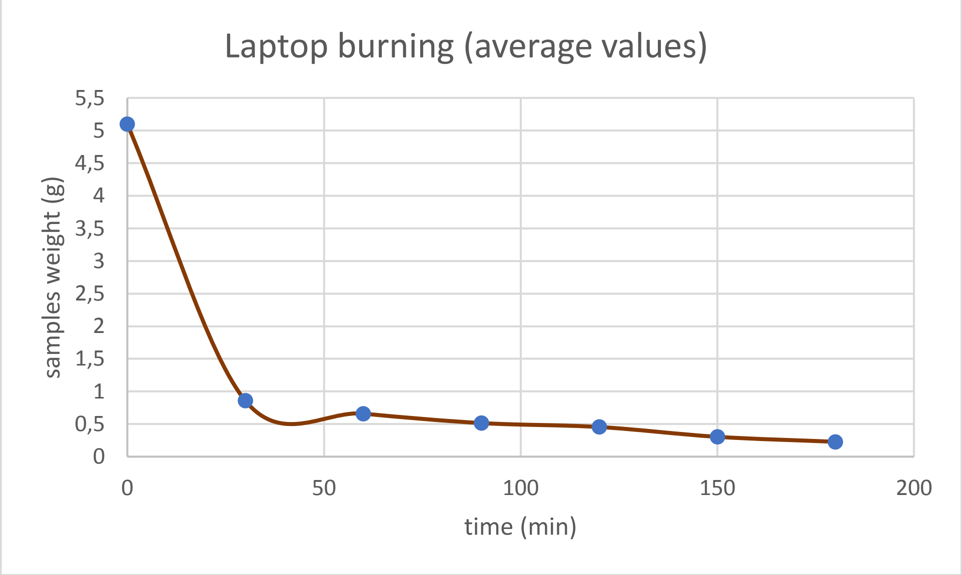


Figure 43 Burning laptops decreasing of weight

In fig.42-45 there are the samples weights trend. As written in procedure A of DIN EN ISO 3451-1, the burning was performed maximum three hours until reaching the mass constancy. For PC screen and TV screen, the samples arrived to the mass constancy after 2 hours of burning. It was calculated that the inorganic content of PC screen plastic was around the 1.5 % of original weight, while TV screen plastic had the lowest inorganic content (0.5% of original weight). Mobile phones and laptop plastic had a bigger inorganic content compared to TV and PC screen, for both it was around 4.5 %

of original weight. Mobile phones ashes arrived to the mass constancy after 2.5 hours of burning, while for laptops the decrease continued until the end of burning in muffle.

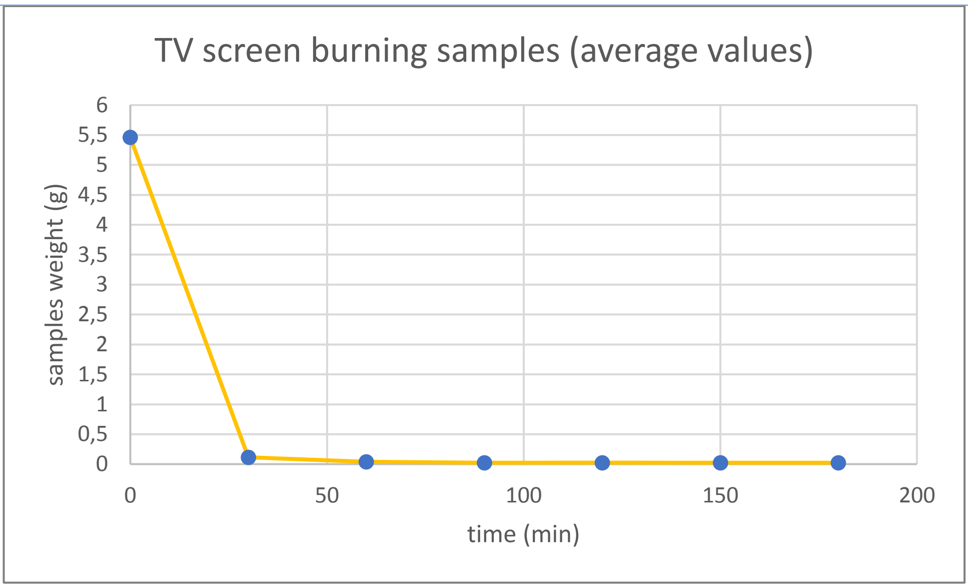


Figure 44 Burning TV screen decreasing of weight

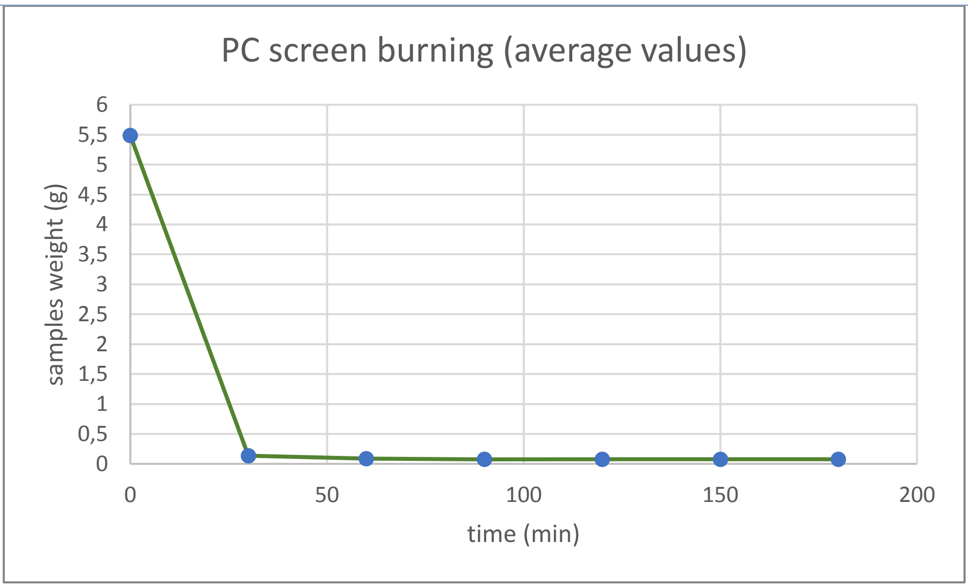


Figure 45 Burning PC screen decreasing of weight

The production of ashes from WEEE plastics was harder in 2 cases:

- For TV screen because of its plastic had a real little amount of inorganic content, only 0.5 %. The TV screen samples achieved mass constancy after 2 hours, but it was requested a big amount of input plastic sample to obtain enough ash samples for analysis. The very low inorganic content of TV screen plastics may be due to the fact that the TV plastics are predominantly composed of non-FR HIPS, with low percentages of ABS (Schlummer, Gruber, Mäurer, Wolz, & van Eldik, 2007).

- For laptop because of the melting process with gas formation was hard to control. For laptop ashes production it was necessary to work slower with preburning step, adding little amounts of plastic during the process (for other WEEE plastics we could start the preburning directly with all the sample). In fact the problem was the volume increase during the heating because all laptop samples doubled their volume in the first part of process. During the preburning large gas bubbles formed inside the sample and their explosion increased the loss of fly ashes (see the next paragraph).

4.1.2 Aqua regia tests for WEEE plastics and ashes

After heating the WEEE plastic samples in the microwave, inside the vessels there were the acid solutions, the Cl in gas phase and the carbonized plastics (fig.46-49).

Figure 46 TV screen after heated aqua regia digestion

Figure 47 PC screen after heated aqua regia digestion

Figure 48 Laptops after heated aqua regia digesiton

Figure 49 Mobile phones after heated aqua regia digestion

After the dilution and filtration of samples, the ICP analysis didn't detect antimony concentrations in the case of PC and TV screen plastic samples. For the mobile phones it was detected a small concentration, around $3.5*10^{-2}$ ppm. Having measured both the dilution volume of the filtered sample and the original weight of the treated plastic, it was possible to calculate that inside mobile phones samples there was a middle antimony content $C_{Sb}=3.2\ mg_{Sb}/kg_{plastic}$ with a standard deviation $\sigma_{Sb}=\pm 1.8\ mg_{Sb}/kg_{plastic}$. The result presents a non-low uncertainty, justified by the fact that the original sample consisted of the plastics derived from 5 different mobile phones. However, it is possible to conclude that from the treatment it was extracted at least 1 $mg_{Sb}/kg_{plastic}$. From the laptops plastic, diluted and filtered solutions with a middle concentration around 6.5 ppm were obtained. Laptops plastics were really reached of Sb and from the calculations it was obtained that $C_{Sb}=765\ mg_{Sb}/kg_{plastic}$ and $\sigma_{Sb}=\pm 86\ mg_{Sb}/kg_{plastic}$. In this case there are excellent prospects of antimony recovering, more than 0.5 g per kg.

In addition to determining the inorganic content of the samples, a big amount of WEEE plastics was burning to obtain an enough ash quantify for aqua regia extraction. In fact, for each sample it was necessary to have 0.5-1 g for extraction process. With lower quantities, ICP analyzes may not produce significant results. In fig.50 there are represented the results obtained with ICP for ashes produced from W.E.E.E. plastics. The first thing that can be observed is that all the samples contained antimony. The ashes are composed exclusively of the inorganic components of starting plastics and it is much easier to extract the substances inside them, also because the solvent mustn't destroy the polymeric bonds. As it could be expected from the results on plastics, laptop ash resulted the richest in antimony (considering the negative value of standard deviation, al least 5 g_{sb}/kg_{ash}).

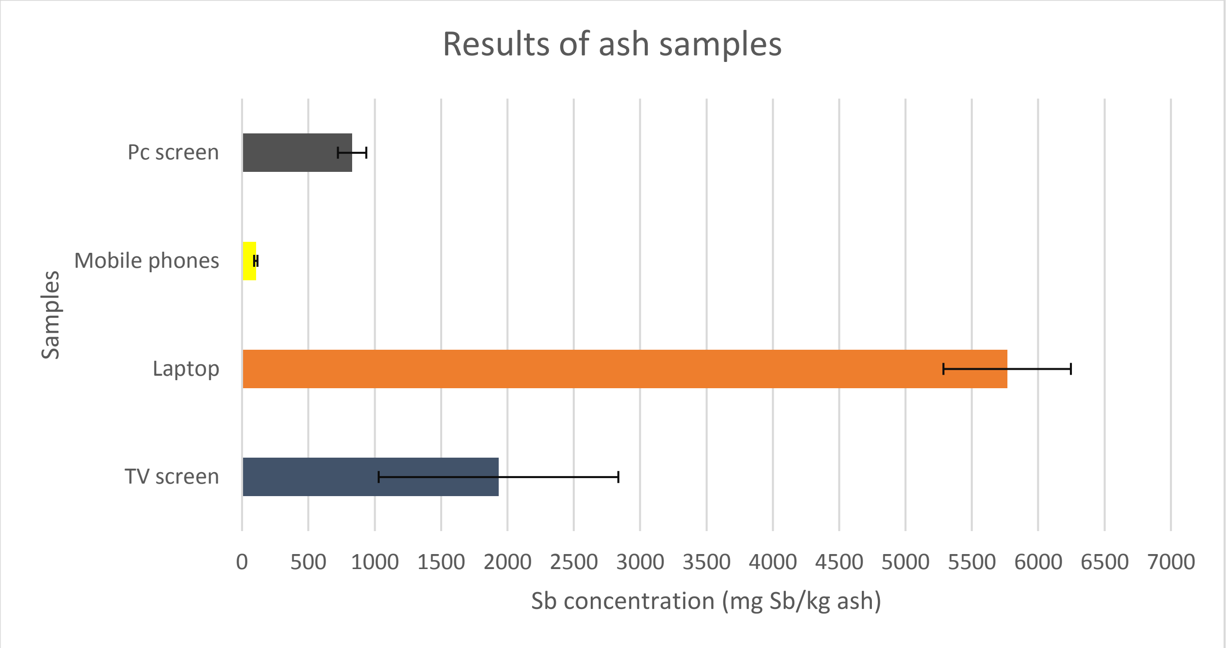


Figure 50 Ash samples antimony content

The samples that produced the lowest result were the mobile phones ashes, less than TV and PC screen inorganic content. The results, shown above as a histogram, are also reported in tab.8.

Table 8 Ash samples antimony content

Ash Samples	average values (mg/kg)	standard deviation
PC screen	829.34	107
TV screen	1593.7	396.5
mobile phones	103.6	12.6
laptops	5766	480.3

If the results obtained from plastics are compared with those obtained from the ashes, we note that PC and TV screen plastics didn't produce results despite the rich antimony content in the ashes. From mobile phones plastics a little antimony quantify was extracted and at the same time inside their ashes ICP detected the lowest antimony concentration (an order of magnitude smaller than the other ashes). For example, TV screen ashes had antimony content ten times bigger than mobile phones ashes, but for original plastic analysis didn't produce good results. Probably the reason is related to the different inorganic content that in TV screen was only 0.5 % of total weight (for PC screen 1.5%). Mobile phones plastics had a 4.5% of inorganic matter and aqua regia attacked more

effectively. Laptops plastics had the best conditions for extraction process: a big amount of antimony and 4.5% of inorganic content (as mobile phones).
Although the ashes contain significant concentrations of antimony, it is plausible that in the combustion process of the original samples there were losses. Having a large loss of fly ash during the combustion process leads to a significant loss of extractable antimony. In tab.9 range values of Sb and other elements content in MSWI incineration residues are reported, according to the overview work of “Allegrini et al.” (Allegrini, et al., 2014) and “Jung et al.” (Jung & Osako, 2009). The ashes values were compared with ores values.

Table 9 comparision of some metal elements contents (mg/kg) in MSWI ashes with ores”

(Allegrini, et al., 2014) (Jung & Osako, 2009)

Element	Bottom ash	Boiler ash	Fly ash	Typical ore
Sb	10-400	200-1000	260-1100	27000
As	1-200	20-60	40-300	1000-40,000
Cu	300-8000	500-1000	600-3200	5000-20,000
Pb	100-14,000	1000-35,000	5300-26,000	300,000-400,000
Sn	2-400	200-700	550-2000	4000

These range values were calculated considering the ashes deriving from mixed MSWI wastes, where the antimony derived from “glasses, textiles and plastics” (Nakamura, Kinoshita, & Takatsuki, 1996). The antimony content in boiler and fly ashes cloud be significantly higher than in bottom ashes. For what concerns the ashes prepared in laboratory, having the antimony ash contents and the inorganic % of plastics, an estimate of antimony content in plastics was calculated (tab.10). These values could be compared with ICP results obtained from plastics digestion only in case of laptops and mobile phones (for aqua regia extraction of PC and TV screen plastics we didn’t have positive ICP results to compare with the estimate values).

Table 10 estimated Sb content in plastics, calculated from Sb content in ashes

	Laptop	Mobile phones	PC screen	TV screen
$Kg_{ASH}/kg_{PLASTIC}$	0.045	0.045	0.015	0.005
$mg_{Sb}/kg_{PLASTIC}$	259.47	4.66	12.44	9.66

For mobile phones, the estimate value 4.66 $mg_{Sb}/kg_{plastic}$ resulted very close to the result obtained for plastic samples extraction. In fact, considering the average value of samples and their standard deviation in absolute value, the antimony extracted was around 3.2+1.8=5 $mg_{Sb}/kg_{plastic}$. In this case, no major losses deriving from the preparation of the ash were highlighted.

For laptops, the estimate value 259.47 $mg_{Sb}/kg_{plastic}$ evidenced that a big amount of antimony was losed during the ash preparation. The content extracted from the original plastic was 765±86 $mg_{Sb}/kg_{plastic}$, about three times higher than the value estimated from the ashes. The difference in these two results could be explain considering the problems faced in the preparation of the laptops ash samples. The increase in volume during the preburning, caused by the formation of gaseous bubbles, contributed to the loss of fly ash. The uncontrollability of the samples allowed the loss of a component of the ashes rich in antimony. For samples of phones and laptops, it is convenient to extract the antimony directly from the plastics, specially for laptops because the analysis showed a big amount of antimony lost during the burning step. The direct extraction on the plastics allowed to recover more antimony per unit of weight.

4.1.3 Aqua regia tests with PET

The last aqua regia tests carried out in the laboratory were extractions from PET, applying the procedure followed for WEEE samples. The different types of PET samples, investigated and listed in materials and methods, were chosen because they well represented the different stages of life of PET within the circular economy:

- The first production of PET (virgin PET in pellets)
- PET before being recycled (shredded and washed PET from veolia)
- PET reused (water and coca cola bottles)

In fig. results are reported. For virgin PET it was obtained an average antimony content C_{Sb}=171.11±7.9 $mg_{Sb}/kg_{plastic}$. This result confirmed that in PET preparation the best antimony quantity was used to catalyze the producing process (Duh,2002). The results for the other samples showed higher standard deviations, justified by the high recyclability of PET. In fact, the plastic bottles were manufactured by mixing virgin PET with recycled PET (for water bottles the average value obtained was 213±38.52 $mg_{Sb}/kg_{plastic}$, while for coca cola bottles it was 163.29±95.2 $mg_{Sb}/kg_{plastic}$). For washed PET, as it is showed in fig.51, an high standard deviation was obtained.

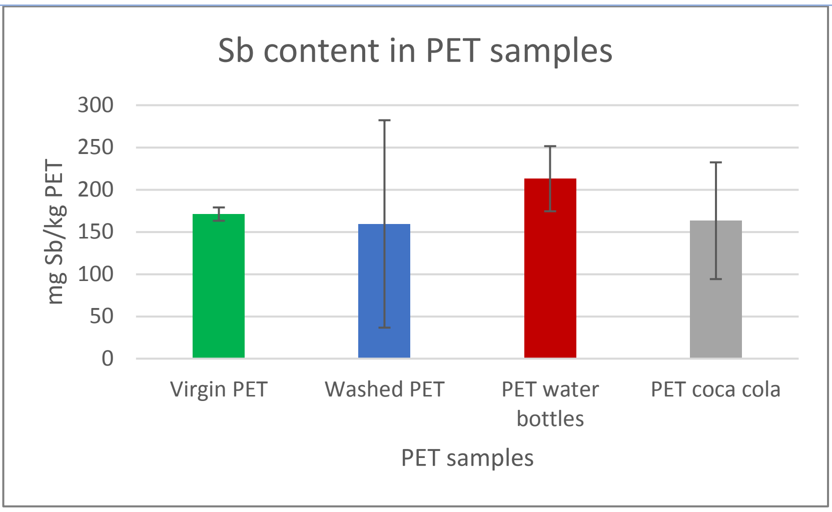


Figure 51 Sb content in PET samples

The washed PET result (157.96±120.64 $mg_{Sb}/kg_{plastic}$) is justified because the analyzed samples contained a mixture of crushed and washed PET, colored and not. This mix of PET didn't yet undergo the real recycling treatments, but it was only preliminarily prepared.

4.2 Tests with HCl

In this paragraph HCl tests are discussed. For WEEE plastics different acid digestions with HCl were performed, using the procedures shown in material and methods(fig):

- Acid digestion of 1 g samples in microwave with 10 ml of HCl 6 M
- Acid digestion of 2 g samples in microwave with 10 ml of HCl 12 M
- Acid digestion of 1 g samples at room temperature and in slight depression with 5 ml of HCl 12 M (incubation time 2 h)
- Acid digestion of 1 g samples at room temperature and in slight depression with 5 ml of HCl 12 M (incubation time 24 h)

The extractions performed with HCl used different conditions, in terms of molarity, temperature, pressure and solid/liquid ratio.

4.2.1PC screen

In fig.52 there are the average antimony contents obtained for PC screen plastic (ABS-HF 380).

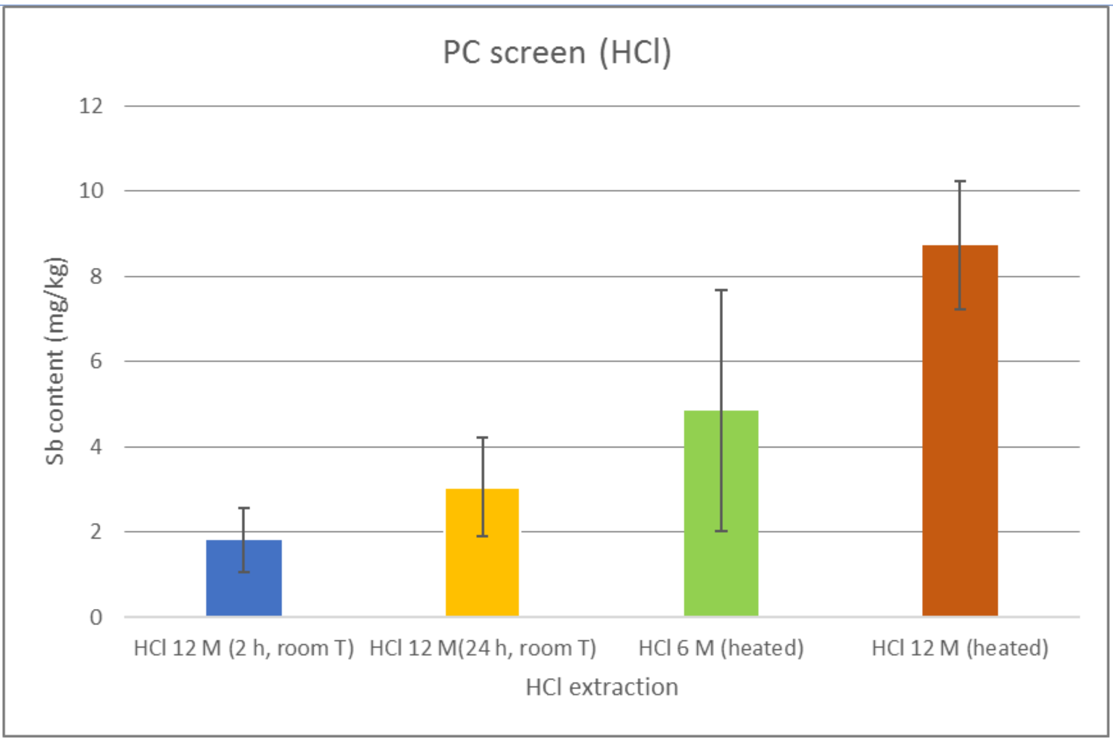


Figure 52 HCl extractions results for PC screen

In all the tests antimony presence was found. Considering the not heated tests, the two extractions gave really close results. After two hours of incubation at room temperature, the filtered and diluted samples had an average antimony content corresponding to 1.82±0.76 $mg_{Sb}/kg_{plastic}$ while the samples prepared with 24 hours of incubation had an average antimony content corresponding to 3.05±1.16 $mg_{Sb}/kg_{plastic}$. A bigger time of incubation permitted to extract around 1 $mg_{Sb}/kg_{plastic}$ more respect the extraction after 2 hours. Although, both tests showed that the exctractions without heat didn't recover a large amount of antimony (the content estimated from ashes was 12.44 $mg_{Sb}/kg_{plastic}$).

The exctration with microwave heat gave better results. Using HCl 6 M, the ICP detected an average antimony about 4.84±2.82 $mg_{Sb}/kg_{plastic}$. Using an HCl solution 6 M with a microwave heating, it was obtained an average exctrated value bigger than not heated tests. Considering the standard deviations values, HCl 12 M without heat and HCl 6 M heated worked at a similar efficiency. Using a solution with higher molarity but without heat, the exctration didn't work well as a heated extraction with a less strong acid solution.

The HCl 12 M exctration, with microwave heating, gave a better result. It was extracted an average value equal to 8.72±1.5 $mg_{Sb}/kg_{plastic}$, the double of HCl 6 M extraction (and with a smaller standard deviation). In this case, an antimony content close to estimated value 12.44 $mg_{Sb}/kg_{plastic}$ was obtained. Work with a 12 M solution and with the help of microwaves duplicated the power of extraction, in comparison to other HCl tests.

4.2.2 TV screen

The exctraction tests for TV screen plastic (monstly HIPS and in less quantity ABS) produced the worst results (lower concentrations extracted, more statistical uncertainties). The real little inorganic content of samples could be the cause. The plastic of TV screen problably was composed more about HIPS, a polymer usually produced without flame-retardants. The small percentage of inorganic content probably derived from a little amount of ABS of which TV screen plastic was composed, i.e. a type of polymeric material containing flame-retardants.

The ICP analysis for samples prepared at room temperature didn’t produce sufficiently positive results to be statistically valid (standard deviations bigger than middle values). In fig.53 there are the results obtained with HCl 6M and 12M, working with microwave.

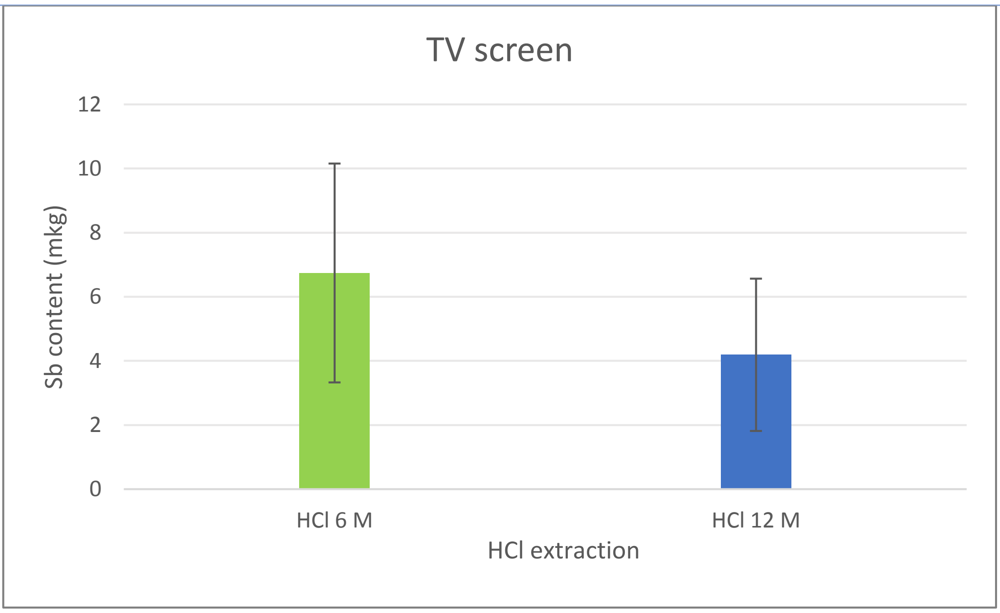


Figure 53 HCl extractions results for TV screen

Both extractions produced low results and they didn’t evidence that the use of a more concentrated HCl solution worked better. The two results are really close, 6.74±3.4$mg_{Sb}/kg_{plastic}$ for HCl 6 M and

4.19±2.37 $mg_{Sb}/kg_{plastic}$ for HCl 12 M (a bigger average value for the extraction with HCl 6M, but in the same time a bigger standard deviation).

4.2.3 Mobile phones

The tests were performed with a mix of six screens coming from old generation mobile phones. The most used plastic for mobile phones is ABS-PC (monstly PC and ABS).

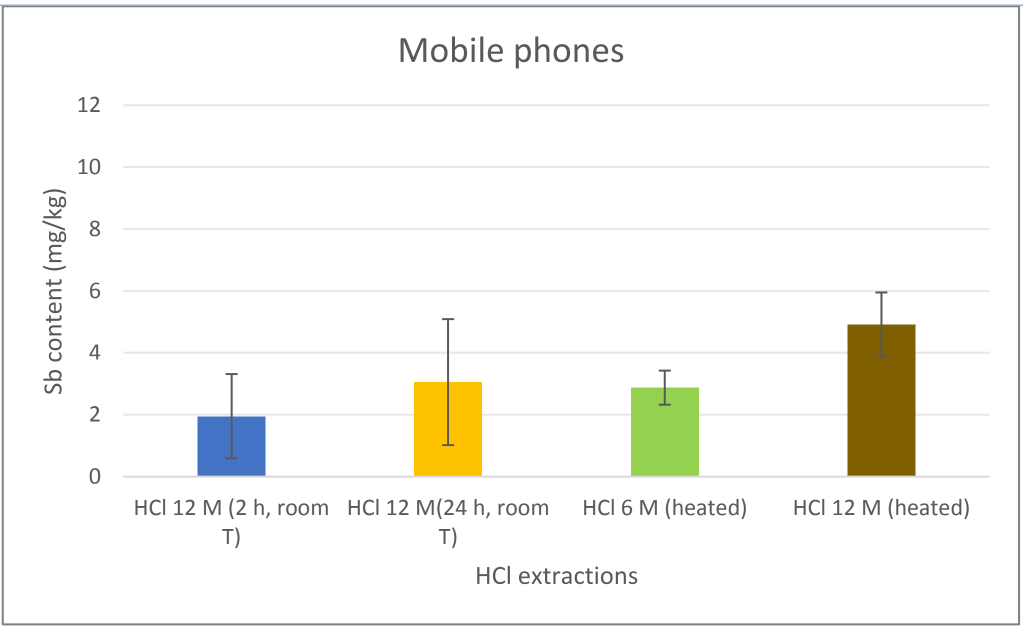


Figure 54 HCl extractions results for mobile phones

In fig.53 there are the results obtained from ICP. Also in this case, the extractions at room temperature didn't show significantly different results, 1.95±1.36 $mg_{Sb}/kg_{plastic}$ after 2 h of incubation and 3.05±2.03 $mg_{Sb}/kg_{plastic}$ after 24 h of incubation. For the microwave extraction with HCl 6 M, the average content extracted was 2.87±0.55 $mg_{Sb}/kg_{plastic}$. Also in this case the use of heat produced a better result, despite having worked with a more diluted acid solution. Comparing the values obtained with HCl 6 M heated and with HCl 12 M not heated (24 h of incubation), the average content extracted for HCl 6 M heated is really close to the 24 h room T value. The big difference is in the standard deviation, an order of magnitude lower for HCl 6 M heated result. A slightly higher amount of antimony was extracted with the HCl 12 M heated test, i.e. 4.91±1.04 $mg_{Sb}/kg_{plastic}$. The small difference between the Sb contents, obtained from the two microwave tests, can be explained considering aqua regia exctrated values (tab.11) The antimony content was basically low inside the samples. Furthermore, the higher uncertainties were related to the number of mobile phones used to prepare the samples. The samples were prepared by shreddering the screens of six different mobile phones.

Table 11 Sb content results for mobile phones

	Average value (mg/kg)
HCl 6 M (heated)	2.87±0.55
HCl 12 M (heated)	4.91±1.04
Aqua regia (heated)	3.02±1.80
Content estimated from ashes	4.66

The samples weren't prepared using the plastic of a single type of mobile phone because it wouldn't have been enough to achieve all the tests. According to the results, HCl 12 M extraction worked better than aqua regia extraction and without carbonising the samples (as for PC and TV screen samples). Furthermore, the Sb content estimated from ashes confirmed the success of the HCl 12 M extraction process.

4.2.4 Laptops

The laptops samples, the richest in antimony, didn't produce good results for not heated tests (0.98±0.98 $mg_{Sb}/kg_{plastic}$ for 2 h incubation extraction and 2.8±2.53 $mg_{Sb}/kg_{plastic}$ for 24 h incubation extraction). In fig.55 there are the average antimony content derived from heating tests.

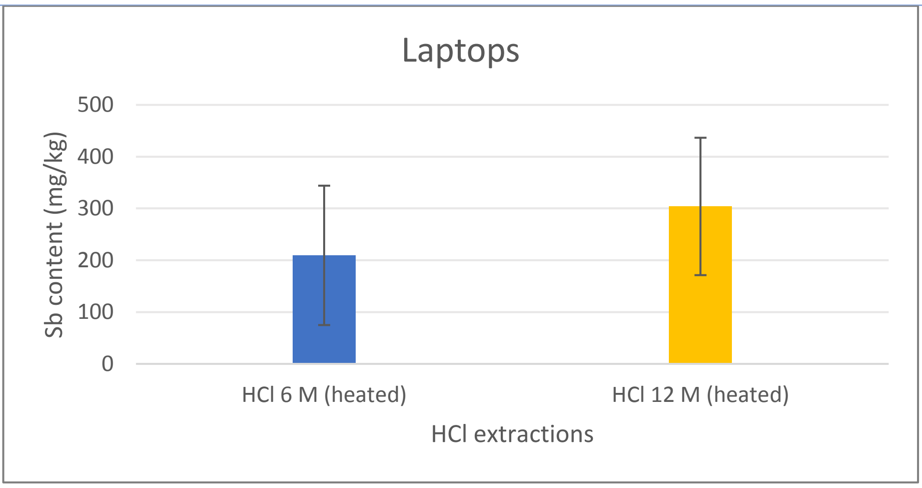


Figure 55 HCl extractions results for laptops

The good results shown in fig. 55 (209.5±134.54 $mg_{Sb}/kg_{plastic}$ for HCl 6 M and 303.94±132.61 $mg_{Sb}/kg_{plastic}$ for HCl 12 M) confirmed that the catalytic effect of heating is essential for an effective extraction. These average extracted values are close to the value estimated from ashes (259.47 $mg_{Sb}/kg_{plastic}$) and the 12 M HCl solution allowed to have a result one third higher than 6 M HCl solution. However, for this type of sample, a much higher quantity of antimony was extracted from aqua regia (765±86 $mg_{Sb}/kg_{plastic}$). Probably a more aggressive solvent was necessary to trigger the decomposition reactions of the laptops plastic polymers which, as already noted, created instability and gas bubbles. The use of HCl 12 M with heat produced a better result compared the recovering from ashes (the estimated Sb content from ashes was lower than that extracted with HCl 12 M.

4.3 Tests with concentrated sulfuric acid

In this paragraph antimony contents extrated from an sulfuric acid concentrated heated solution will be showed and compared with aqua regia and HCl heated extration. All the extractions requested a bigger cost, due to the higher complexity in filtering samples. In fact, the sulfuric acid melted completely the plastics, creating a solution with a dense solid content.

4.3.1 PC Screen

The average antimony content obtained from sulfuric acid (3.71±0.37 $mg_{Sb}/kg_{plastic}$) was lower compared to the value obtained with HCl 12 M (fig.56)

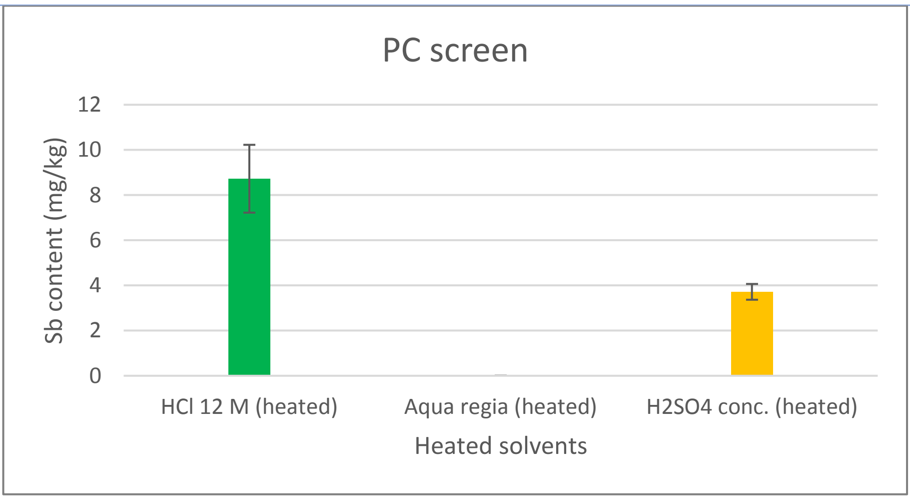


Figure 56 Heated acid solvent results comparison for PC screen

Extraction with HCl 12 M worked better, allowing savings in terms of filtration costs, both in terms of solvent used (H_2SO_4 was used concentrated, while HCl was used after a dilution with deionized water).

4.3.2 TV screen

As for PC screen, the H_2SO_4 didn't work better than HCl 12 M extraction (fig.57). The average antimony content, extracted with H_2SO_4, presented a high degree of statistical uncertainty (5.78 ± 4.34 $mg_{Sb}/kg_{plastic}$).

The result confirms what was said in the paragraph 3.2.2.

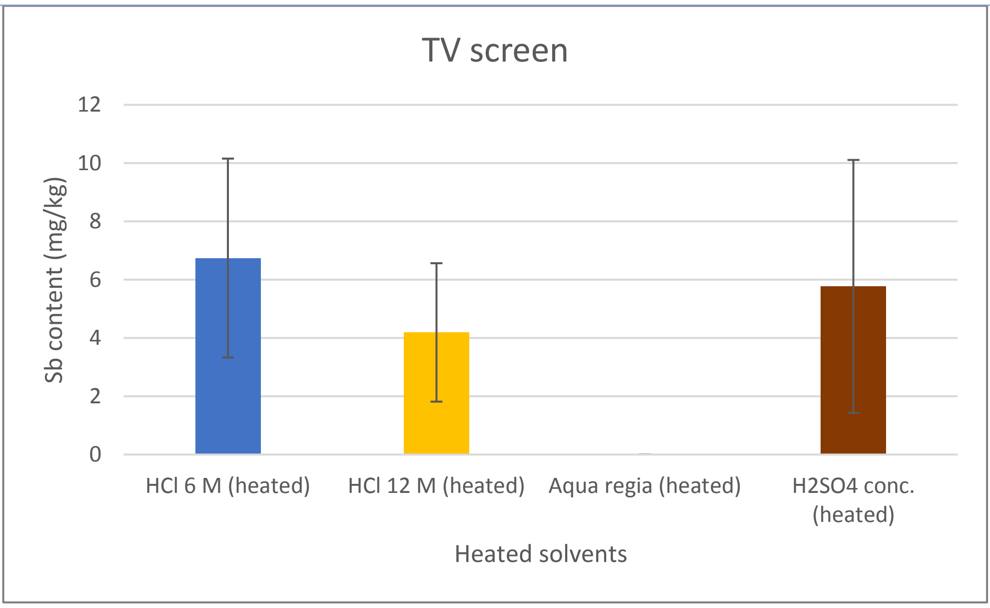


Figure 57 Heated acid solvents results comparison for TV screen

4.3.3. Mobile phones

For mobile phones results, the considerations set out for the two previous samples are valid. The average antimony content obtained with H_2SO_4 was 3.85 ± 2.74 $mg_{Sb}/kg_{plastic}$ (fig.58)

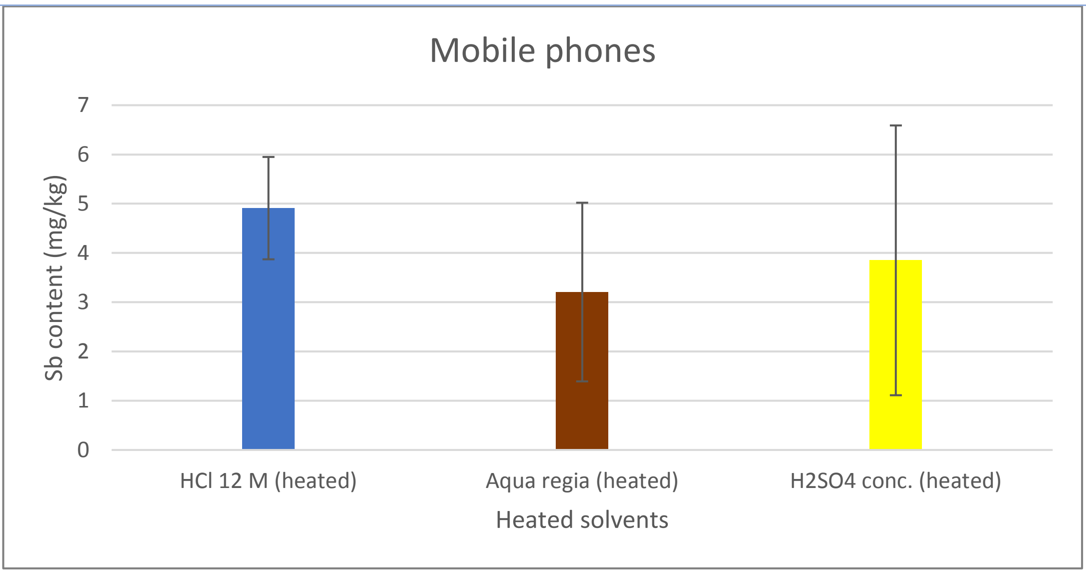


Figure 58 Heated acid solvents results comparison for mobile phones

4.3.4. Laptops

The speech for laptops plastic is different. With H_2SO_4 extraction a value really close to aqua regia extration was obtained (767.41±106.29 $mg_{Sb}/kg_{plastic}$). In this case, unlike the other samples, it is clear that both aqua regia and sulfuric acid worked more efficiently than HCl 12 M (fig.59). However, it was more convenient to work with aqua regia, due to lower filtration costs.

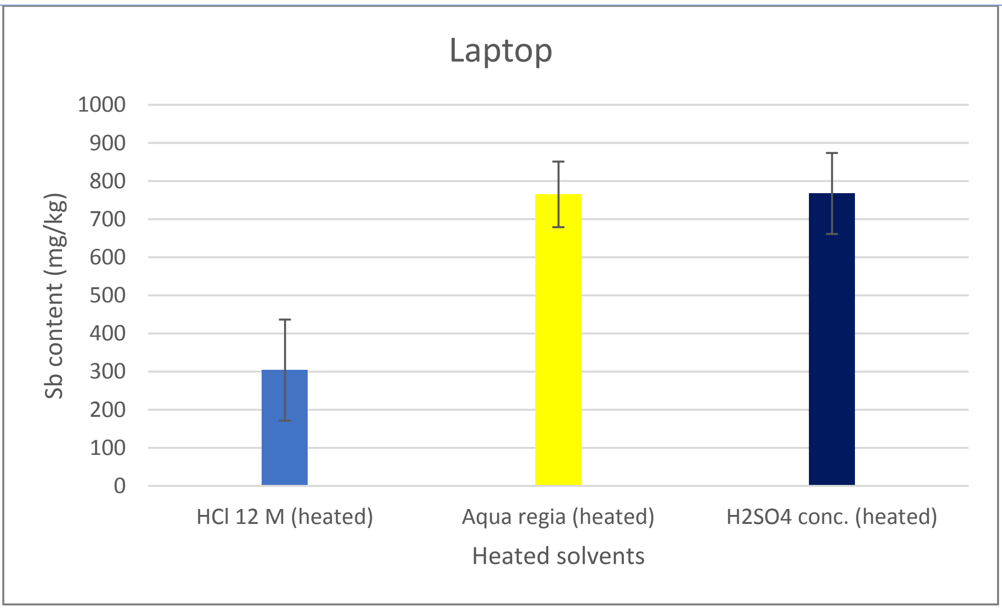


Figure 59 Heated acid solvents results comparison for laptops

5. Conclusions

The aim of this thesis work was to investigate the potential of antimony extraction from plastics materials. Considering the main uses of antimony in polymers and the possible fates of plastics and WEEE, several extraction tests were carried out with acid solvents.

During WEEE and PET extraction tests with aqua regia, the acid solvent completely carbonized the samples. For samples rich in antimony, as the plastic of laptops, it has shown excellent recovery yields. However, it wasn’t able to extract antimony in samples with low content as PC and TV screen. The extractions carried out in the various PET samples have shown excellent results, demonstrating that a large part of the antimony trioxide previously added is potentially recoverable from PET. Ashes deriving from WEEE plastics were prepared and treated with heated aqua regia. Plastics with low antimony content (as TV screen and PC screen samples) can become a secondary source of antimony and other materials with economic interest, after being subjected to energy recovery. The antimony losses, highlighted by analyzing the results of laptops ashes, showed how much antimony bottom ash can contain.

Extractions with 12 M hydrochloric acid in microwave oven showed good results. Using heated hydrochloric acid allowed to extract antimony from the samples without destroying them completely. Hydrochloric acid can be a good solution to recover the antimony from plastics, without having to completely destroy them (for the treated plastics it could then be evaluated possible reuse). The use of hydrochloric acid without proper heating didn’t lead to positive results. For laptops plastics, 12 M hydrochloric acid allowed a much more efficient extraction compared to that obtained from the ashes. In fact, more than half of the extractable antimony was lost in the preparation of laptops ashes, due to the loss of fly ash and gas.

Extractions with concentrated sulfuric acid were the hardest to complete. Sulfuric acid is extremely aggressive towards organic substances and its effect, combined with microwave heating, has caused the complete dissolution of plastic samples. The plastic samples were melted and charred. As for the results obtained from ICP analyzes, the use of sulfuric acid showed no advantages compared to other solvents. For laptops plastics, the antimony content extracted was almost the same as compared to the one obtained with aqua regia. For other WEEE samples, 12 M hydrocloric acid solution worked better, managing to extract with lower costs and higher efficiency.

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