

Characterization of Elements in the Printed Circuit Boards of Television to Enhance Managing E-Waste through Resource Recovery

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Abstract: The environmental effects of e-waste disposal are drawing increasing attention throughout the world. The crude recovery methods being used in the developing world expose people to a host of toxic materials and contaminants. The objective of this study was to characterize electronic waste emanated from television printed circuit boards for their elemental composition to enhance heavy metal recovery from the boards. Printed Circuit Boards (PCBs) of about 5kg, extracted from obsolete television sets were ground and sieved to obtain 2 mm particle size. The processed PCB was soaked in 1 M, 3 M, 5 M and 7 M nitric acid solutions for varying period of time (0 h, 12 h, 24 h and 48 h). The PCB characterization was done by analysing the leachates using Inductively Couple Plasma - Mass Spectrometer (ICP-MS 2000). Varying quantities of up to 70 elements were found on the PCB. Copper ($236\ 190.00 \pm 2.31\ \text{mg}\cdot\text{kg}^{-1}$) was found to be the most abundant metal followed by aluminum ($27\ 148.00 \pm 1.1\ \text{mg}\cdot\text{kg}^{-1}$), iron ($97\ 010 \pm 5.00\ \text{mg}\cdot\text{kg}^{-1}$), lead ($33\ 513 \pm 2.14\ \text{mg}\cdot\text{kg}^{-1}$), tin ($6\ 665.20 \pm 0.74\ \text{mg}\cdot\text{kg}^{-1}$) and zinc ($8\ 948.00 \pm 0.68\ \text{mg}\cdot\text{kg}^{-1}$). The concentrations of aluminum, nickel, lead and titanium using 1 M, 3 M, 5 M and 7 M concentrations of nitric acid were found to be statistically significant across the various time intervals (0 h, 12 h, 24 h, and 48 h). Rare earth elements were found in trace quantities. The results of this study are useful in management of valuable heavy metals present in e-waste through resource recovery thereby reducing the toxic hazardous waste getting into the waste stream.

[Oyelami H.I., Hamed T.B. and Sridhar M.K.C. **Characterization of Elements in the Printed Circuit Boards of Television to Enhance Managing E-Waste through Resource Recovery.** *Nat Sci* 2016;14(10):114-118]. ISSN 1545-0740 (print); ISSN 2375-7167 (online). <http://www.sciencepub.net/nature>. 18. doi:[10.7537/marsnsj141016.18](https://doi.org/10.7537/marsnsj141016.18).

Keywords: E-waste; Heavy metals recovery; Obsolete television sets; Printed circuit board; Rare earth elements

1. Introduction

Electronic devices form a complex mixture of materials and components, often containing several hundreds of different substances, many of which are toxic and create serious pollution upon indiscriminate disposal (Sharma and Pathak, 2012). These include heavy metals such as mercury, lead, cadmium, chromium and flame retardants such as poly-brominated biphenyls (PBB) and poly-brominated diphenylethers (PBDEs). In addition to various hazardous materials, e-waste also contains many valuable and precious materials. Using the personal computer (PC) as an example, a normal Cathode Ray Tube (CRT) computer monitor contains many valuable substances along with many toxic components (STEPINITIATIVE, 2014). That is, e-waste is chemically and physically distinct from other forms of municipal or industrial wastes as it contains both valuable and hazardous materials (Cobbing, 2008). A mobile phone can contain over 40 elements including base metals (e.g. copper and tin), special metals (e.g. cobalt, indium and antimony), and precious metals (silver, gold, palladium and so on).

The populated PCBs, constituting 3 to 5 % by weight of total e-waste, have rich value of metals such as silver, gold, palladium, platinum, tantalum and

other metal in trace amounts. Copper, which is used to form the electrical circuit on the Printed Circuit Boards (PCBs), is the dominant metal species (Hall and Williams, 2007; Zhou and Qui, 2010). Their recovery requires professional skills and high cost equipment. The lack of knowledge, affordable logistics and greed for quick money motivates non-formal sector to employ unhygienic and unscientific methods for recovery of valuable metals such as Cu, Ag, and Au and so on (Chatterjee and Krishna, 2009). Discarding recoverable metals is energy inefficient and liable to causing environmental health hazards. Energy savings from recovering metals are high when compared to mining new material; the energy savings for aluminum is 95 %, copper 85 %, steel 74 %, lead 65 %, and zinc 60 %. According to Nnorom et al. (2008), recovering other materials such as paper and plastics can reduce energy usages by 64 % and 80%, respectively.

As a result of the increasing availability of new electronics, along with the higher number of products built with shorter life spans, there is presently an explosion in the quantity of electronic waste being generated globally (Pucke et al., 2002). Disposal of these e-wastes is an emerging global environmental issue, as these wastes have become one of the fastest

growing waste types in the world (Sharma and Pathak, 2012; Willner and Agnieszka, 2013). The crude recovery methods used at developing world recycling facilities expose unskilled workers, who are often children, to a host of toxic materials and contaminants used in the manufacture of electronics. Previous crude e-waste recycling practices (Mehra, 2004; Leung et al., 2008; Osuagwu and Ikerionwu, 2010). The widely-reported practice of burning cables and printed wiring boards to recover the metals they contain is known to release polychlorinated dibenzodioxins and furans (PCDDs and PCDFs) that can be toxic in even small doses. The combustion can also lead to the release of dust and fumes from the beryllium present. Inhalation can cause the incurable pulmonary disease berylliosis, the symptoms of which can in some cases begin to appear years after the last exposure (Holloway, 2012).

Hence, the need to characterize e-waste for their elemental composition is highly essential, to ensure appropriate handling and management of these toxic and precious waste streams. In this study, electronic waste in the form of PCBs was characterized for their elemental composition to find out the possibility of extracting some of the recyclable elements present therein for reuse.

2. Material and Methods

Waste PCBs (5 kg) of various brands of Televisions, collected randomly from different electronics repairer's workshops, was ground with hammer mill. Size reduction of the waste PCBs was done to liberate metals from other polymer contents and to increase the efficiency of extraction of metals through the metal – acid contact. The ground PCBs were then sieved with 2 mm sieve to ensure homogeneously mixed particle size that was used in this study (Fig. 1). Four different concentrations of nitric acid were prepared i.e. 1 M, 3 M, 5 M, and 7 M. Five grams of ground PCBs was weighed with analytical balance (Techmel LP123A) and soaked in 100 ml of the various nitric acid concentrations prepared. The solution was left for: 0 h, 24 h, and 48 h. The extractants obtained from the above were filtered through What man Filter Paper No 1(110 mm size). The filtrate obtained from each solution was then analyzed for its elemental composition, using an instrumental method: Inductively Couple Plasma - Mass Spectroscopy, using ICP-MS 2000 spectrometer.

The probable chemical reactions involved in the dissolution process are given in the equations below:

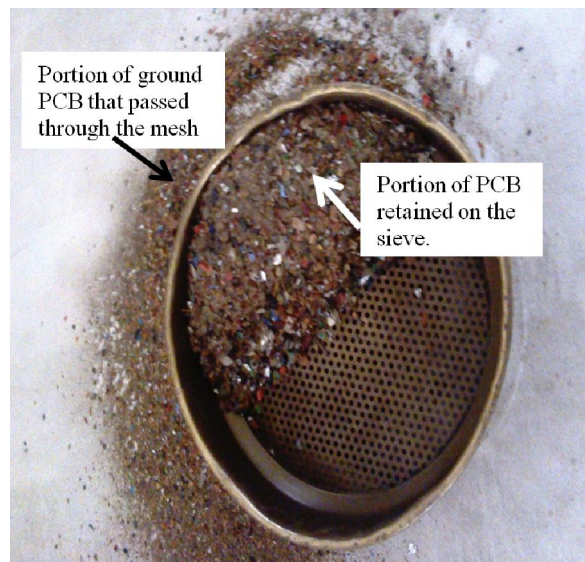
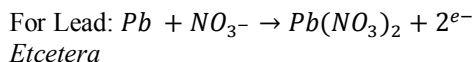
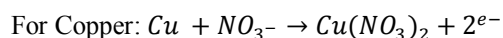


Fig. 1. Sieving with homogeneously mixed particle of ground PCBs

3. Results and Discussions

The results of the e-waste sample analysis showed that up to 70 elements (comprising metals and non-metals) could be found in a typical PCB of television. As shown in Tables 1 to 5, some of these elements were categorized according to the classification of elements in the periodic table viz. metalloids, alkali metals, alkaline earth metals, transition metals, rare earth metals and precious metals. Previous study revealed that up to 60 elements (both valuable and toxic) from the periodic table could be found in complex electronics (StEPINITIATIVE, 2014). Kitsara (2014) earlier discussed the presence of rare earth elements in his study, although this class of elements was found in trace quantities. Waldir et al. (2014) also reported that PCBs consisted of approximately 26 % metal, made up mainly of copper, lead, aluminium, iron and tin, as well as other heavy metals such as cadmium and nickel.

Copper ($236\ 190.00 \pm 2.31 \text{ mg}\cdot\text{kg}^{-1}$) was found to be the most abundant metal in the PCB samples followed by lead ($33\ 513 \pm 2.14 \text{ mg}\cdot\text{kg}^{-1}$), aluminum ($27\ 148.00 \pm 1.1 \text{ mg}\cdot\text{kg}^{-1}$), calcium ($26\ 060.00 \pm 2.28 \text{ mg}\cdot\text{kg}^{-1}$), nickel ($6\ 801.20 \pm 5.38 \text{ mg}\cdot\text{kg}^{-1}$) and barium ($1\ 233.80 \pm 3.11 \text{ mg}\cdot\text{kg}^{-1}$). The concentrations of these elements corroborate the findings reported by other authors: copper (Menetti and Tenório, 1995; Iji and Yokoyama 1997), aluminium (Wang et al., 2005; Das et al., 2009; Oliveira et al. 2010) and zinc (Feldman, 1993; Yoo et al., 2009). Meanwhile, the values obtained for these elements were higher than what obtained by several researchers: copper (Das et al.,

2009; Hino et al., 2009), lead (Das et al., 2009; Hino et al., 2009; Yoo et al., 2009; Oliveira et al. 2010; Waldir et al., 2014) and, nickel and iron (Das et al., 2009; Marco et al., 2008; Oliveira et al., 2010).

Table 1. Optimal time and concentration of transition metals leached from printed circuit boards of television ($\text{mg}\cdot\text{kg}^{-1}$)

Element	Element Concentration ($\text{mg}\cdot\text{kg}^{-1}$) (Mean \pm SD)	Optimal Time (h)	Optimal Concentration (Mole)
Cu	236190.00 \pm 2.31	48	3
Ni	6 801.20 \pm 5.38	24	3
Al	27 148.00 \pm 1.1	48	5
Zn	8 948.00 \pm 0.68	48	3
Fe	97 010.00 \pm 5.00	48	1
*Ag	31.20 \pm 0.57	12	3
Hg	0.02 \pm 0.00	0	1
*Au	100.00 \pm 2.28	12	3
*Pt	0.02 \pm 0.001	0	3
*Pd	1.42 \pm 0.31	24	1

**Precious metals*

Table 2. Optimal time and concentration of alkali metals leached from printed circuit boards of television ($\text{mg}\cdot\text{kg}^{-1}$)

Element	Element Concentration ($\text{mg}\cdot\text{kg}^{-1}$) (Mean \pm SD)	Optimal Time (h)	Optimal Concentration (Mole)
Li	200 \pm 5.57	48	1
Na	758.00 \pm 6.88	12	1
K,	244.00 \pm 0.49	12	1
Rb,	0.44 \pm 0.03	12	1

Table 3. Optimal time and concentration of alkaline earth metals leached from printed circuit boards of television ($\text{mg}\cdot\text{kg}^{-1}$)

Element	Element Concentration ($\text{mg}\cdot\text{kg}^{-1}$) (Mean \pm SD)	Optimal Time (h)	Optimal Concentration (Mole)
Be	0.01 \pm 0.00	0	1
Mg	1 400.00 \pm 2.84	12	3
Ca	26 060.00 \pm 2.28	12	3
Sr	58.20 \pm 3.88	48	7
Ba	1 233.80 \pm 3.11	48	7

Table 4. Optimal time and concentration of metalloids leached from printed circuit boards of television ($\text{mg}\cdot\text{kg}^{-1}$)

Element	Element Concentration ($\text{mg}\cdot\text{kg}^{-1}$) (Mean \pm SD)	Optimal Time (h)	Optimal Concentration (Mole)
B	285.00 \pm 1.41	12	1
Si	728.60 \pm 4.02	12	1
Ge	0.08 \pm 0.01	12	1
As	600.00 \pm 1.99	0	5
Sb	400.00 \pm 1.42	48	1
Te	0.30 \pm 0.14	0	3

Table 5. Optimal time and concentration of other metals leached from printed circuit boards of television ($\text{mg}\cdot\text{kg}^{-1}$)

Element	Element Concentration ($\text{mg}\cdot\text{kg}^{-1}$) (Mean \pm SD)	Optimal Time (h)	Optimal Concentration (Mole)
Ga	2.44 \pm 0.06	12	1
In	0.70 \pm 0.14	0	1
Sn	6 665.20 \pm 0.74	0	3
Tl	0.15 \pm 0.04	24	1
Pb	33 513.00 \pm 2.14	12	7
Bi	600.00 \pm 2.84	48	1

In contrary to the major observation, tin was found lower than all previous studies carried out in other (Creamer, 2006; Das et al., 2009; Hino et al., 2009; Oliveira et al. 2010). The variation can be explained in terms of wide range of board types used, the different characterization methods used by the various authors and the change in the composition of PCBs over the years. Gold and silver were found very low as indicated that the concentration of these metals had declined over time (Waldir et al., 2014). Though generally classified as hazardous waste, all the elements characterized were less than the maximum permitted concentration set up by EPA legislation (Waldir et al., 2014).

While using various concentrations of nitric acid: 1 M, 3 M, 5 M and 7 M, the quantity of elements characterized were found to be varied significant ($p < 0.05$) across the various time intervals (0 hour, 12 hours, 24 hours, and 48 hours of contact (Table 6). The quantity of zinc was found to be optimal at 48hours (when compared to other time intervals) for 3 M concentration of nitric acid used. It was observed that nitric acid concentration affected the quantities of copper, iron and lead leached. Copper, iron and tin concentrations were observed to be optimal with reduction in soaking time as nitric acid concentration increased.

That is, the increase in nitric acid concentration resulted in decrease in quantity of tin obtained. Mercury was found in low quantities and its quantity was observed to decrease as nitric acid concentration increased. Also, elements found in trace quantities were majorly rare earth elements. Lead, barium and manganese were optimally obtained at 7M concentration of nitric acid. Furthermore, it was observed that low concentration of nitric acid seemed to favour the leaching of the halogens and most of the rare earth elements. Mercury, platinum, rhenium, rhodium, tantalum, tellurium, zirconium, silicon, germanium, cesium, beryllium, scandium, in other classes of elements were also observed to behave similarly. observed maximum in the pine forest as compared to the oak forest in the present study (Table

4), indicating diverse taxonomic vegetation in the pine forest.

Time Interval (h)							
Element Classification (mg·kg ⁻¹)	0 h	12 h	24 h	48 h	F value	P value	
Metalloids	97.69±1.68	180.00±5.93	180.00±5.93	180.00±5.93	1.28	0.40	
Alkali Metals	106.21±4.27	120.00±2.28	120.00±2.28	120.00±2.28	0.16	0.92	
Alkaline Earth Metals	1692.60±2.41	5572.30±3.20	4441.20±4.08	2768.30±4.47	276.36	0.01	
Transition	2817.50±2.90	8228.60±1.85	8147.10±1.70	10465.00±2.47	2000.00	0.01	
Halogens	261.60±7.20	-	-	-	21.82	0.01	
Other Metals	2552.30±3.85	4653.40±1.87	5688.00±1.82	5171.50±1.20	338.78	0.01	
Rare Earth	0.23±0.05	46.26±2.99	46.25±2.98	46.25±2.98	2.67	0.18	
Heavy Metals	7817.00±3.34	21938.00±2.63	22291.00±1.90	27088.00±2.02	326.03	0.01	
Precious Metals	4.14±0.46	21.87±4.81	20.00±5.66	20.00±5.66	6.29	0.05	

4. Conclusion

Copper was found to be the most abundant metal in the mixed printed circuit board samples of various television. The board also contained lead, aluminium, calcium nickel and barium in various quantities. There was high disparity in the levels of elements contained in the printed circuit boards of television found in different country with tin (Sn) content of Nigerian boards being the least. Almost all the elements characterized were less than maximum permitted concentration according to EPA legislation, indicating that Nigerian guidelines need to be established to ensure the classification of these elements as toxic or hazardous material. For process optimization, the quantities of heavy metals obtainable from characterization of the circuit board depend on time of soaking of analyte in nitric acid and concentration of the acid. Generally, low concentration of nitric acid increased the levels of the halogens and most of the rare earth elements.

Acknowledgements:

The authors wish to express their profound gratitude to Mr. Adejumo Mumuni of the Department of Environmental Health Sciences who assisted in data analyses.

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9/16/2016