Hazardous pollutants generated by 1997-1998 generation of printed circuit boards

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Abstract. Due to the high quantity of printed circuit boards waste generated in the last years, it is imperative to quantify their environmental impact and to find recycling solutions. In order to quantify the environmental impact of 1997-1998 generation of printed circuit boards, a leaching test was performed. The following parameters were determined: metals, fluoride, chloride, sulfates, phenol index, dissolved organic carbon, total organic carbon, suspended solids, BTEXs, PCBs and petroleum products. The analyses were performed using sensitive, high performance analytical techniques. The results were compared with those stipulated in the legislation in force in order to identify the appropriate waste category for their storage. The values obtained for Cu, Ni, Pb, Sb and Zn are higher than the maximum admitted levels for their acceptance at landfills for inert waste. While the values of Cu and Zn are decreasing from 51.6 to 4.03 mg/kg for Cu and from 23.6 to 8.79 mg/kg for Zn, the values of Ni and Pb are increasing from 0.75 to 1.55 mg/kg for Ni and from 8.72 to 34.0 mg/kg for Pb from 1997 to 1998. These results show that finding a solution for the recycling 1997-1998 generation of printed circuit boards is being mandatory.

Keywords: WEEE, printed circuit boards, leaching, metals

1. Introduction

In the last decades, due to the evolution of human society, the request for new technology has increased. The technological development of Electrical & Electronic Equipment caused an increase in standards but a decline in lifespan [1] generating a huge amount of waste (WEEE). According to the European Commission, Waste Electrical & Electronic Equipment (WEEE) is a complex mixture of materials and components which requires the use of scarce and expensive resources and can cause major environmental and health problems [2]. Due to the hazardous materials (ferrous metals, non-ferrous metals, glass, plastics and other materials) from WEEE composition, their treatment should be performed properly to avoid important damages to both humans and the environment [3, 4]. Besides the pollution of the environment, the production of modern electronics requires the use of expensive resources: around 10% of total gold worldwide, copper, aluminum, silver, palladium and other metals, which can be recovered from WEEE [2, 3, 5-8]. It is approximated that 17 million of computers are discarded annually in the world due to malfunctioning equipment or because technologies become obsolete and approximately 51 million kilograms of CPU waste are discarded yearly [9]. A proper manipulation of these WEEE will reduce the leaching of the hazardous pollutants in the environment and also increase the efficacy of the recovery techniques.

The purpose of this study is to reveal the potential harmful pollutants released by WEEE from 1997-1998 generation printed circuit boards, stored unproperly in open air. To achieve this goal, a leaching test was performed on six printed circuit boards from 1997, 1998 and 2008. The 2008 printed circuit boards data should give an idea regarding the evolution of the pollutants in time with the improvement of fabrication techniques. The results were compared with the leaching values provided by Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC [10].

2. Experimental

Sample and preparation. 6 samples of printed circuit boards were gently washed several times with ultrapure water and dried in open air. After dryness, the samples were weighted and immersed in ultrapure water respecting the ratio L(liquid)/ S(solid) = 10 l/kg and shacked for 24h. The water was collected and analyzed.

Materials and methods

Metals. Measurements were carried out using an Inductively Coupled Plasma Mass Spectrometer Perkin Elmer ELAN® DRC II ICP-MS according to EN ISO 17294-2:2017. The quality control was assured using a certified reference material NIST 1643e from NIST.

Mercury. Measurements were carried out using a Mercury Analyzer Teledyne Leeman Labs, Hydra-AF according to EN ISO 17852:2008. The quality control was assured using a certified reference material Mercury Hg CertiPUR Suprapur 10 % from Merck.

Fluoride. Chloride. Sulfates. Measurements were carried out using an Ion Chromatography Methrom IC 761 Compact with a METROSEP A SUPP 5-100 separation column and a chemical suppression and conductivity detector according to EN ISO 10304-1:2009. The quality control was assured using a certified reference material SPS-NUTR WW1, Waste Water nutrients – Level 1 from LGC Standards.

Phenol index. Measurements were carried out using an UV/VIS Spectrophotometer Perkin Elmer Lambda 25 according to ISO 6439:2001/C91: 2006. The quality control was assured using a certified reference material Total Phenolics – WP QC1134 from Sigma Aldrich.

Dissolved organic carbon. Total organic carbon. Measurements were carried out using a TOC analyzer Analytic Jena Multi N/C 2011S according to EN 1484:2001. The quality control was assured using certified reference materials: Total organic carbon QC3308, TOC100 from Fluka and MR Sangamon-03 from Environment Canada.

Suspended solids. Measurements were carried out using an analytical balance Partner RADWAG XA60/220 according to EN 872:2005. The quality control was assured using a certified reference material QC1298 -1G Residue suspended –constant value from Sigma Aldrich.

BTEXs. Measurements were carried out using a Gas Chromatograph with Mass Spectrometer 5975B and an Agilent HP-5ms (5%-phenyl)-methylpolysiloxane non-polar capillary column according to ISO 11423-1:2000. The quality control was assured using BTEX in Water – AK Methods from LGC Standards.

PCBs. Measurements were carried out using an Gas Chromatograph with Electron Capture Detector GC-ECD Agilent 6890 N with a Agilent 19091J-413 HP-5 (5% Phenyl 95% Methyl Siloxane) capillary column according to EN ISO 6468:2000. The quality control was assured using the following certified reference materials: Pesticides 1 in Water – Low Level QC1321 and Pesticides 2 in Water – Low Level QC1491 from Sigma-Aldrich.

Petroleum products. Measurements were carried out using a Gas Chromatograph with Flame Ionization Detector GC-FID 7890A Agilent Technologies and an Agilent HP-5, 5% Phenyl 95% dimethylpolysiloxane non-polar capillary column according to EN 9377-2:2002. The quality control was assured using a certified reference material TPH in Water QC1800 from Sigma Aldrich.

3. Results and discussion

The leaching values are presented in Table 1 and the leaching parameters for organic compounds are presented in Table 2. The values obtained for 1997, 1998 and 2008 printed circuit boards were compared with the values specified in the Council Decision of 19 December 2002 for waste acceptable at landfills for inert waste and landfills for hazardous waste. As it can be seen from Table 1, the values obtained for some of the metals (As, Ba, Cd, Cr, Hg, Mo, Se), fluorides, chlorides, sulphates, phenol index, dissolved organic carbon and total dissolved substance are under the maximum values specified by the Council Decision for accepting these printed circuit boards at landfills for inert waste. The values obtained for Cu, Ni, Pb, Sb, Zn are higher than the maximum values specified by the Council Decision to be acceptable for deposit these printed circuit boards at landfills for inert waste but smaller than the limit values specified for the acceptance at landfills for hazardous waste. Due to these values, according to the Council Decision of 19 December 2002, the studied printed circuit boards can be only deposit at landfills for hazardous waste.

Comparing the mean values obtained for Cu, Ni, Pb, Sb, Zn from 1997, 1998 and 2008 printed circuit boards (Figure 1) it can be concluded that:

- Cu – decreases significantly from 1997 to 1998 printed circuit boards (approx. 89%), for 2008 printed circuit boards its values is under the maximum value specified in the Council Decision for accepting the printed circuit boards at landfills for inert waste;
- Ni – it slowly increases from 1997 to 2008 printed circuit boards;

- Pb – increases significantly from 1997 to 1998 printed circuit boards and decreases for 2008 printed circuit boards near the maximum value specified in the Council Decision for accepting the printed circuit boards at landfills for inert waste;
- Sb – for 1997 and 1998 printed circuit boards, its values are under the maximum value specified in the Council Decision for accepting the printed circuit boards at landfills for inert waste and increases over this value for 2008 printed circuit boards;
- Zn – it value decreases from 1997 to 2008 printed circuit boards but its values are still higher then the maximum value specified in the Council Decision for accepting the printed circuit boards at landfills for inert waste.

The values obtained leaching parameters for organic compounds (total organic carbon, polychlorinated biphenyls and petroleum products) from all investigated printed circuit boards are smaller then then the maximum value specified in the Council Decision for accepting the printed circuit boards at landfills for inert waste.

4. Conclusions

6 printed circuit boards from 1997, 1998 and 2008, two of each year, were investigated in order to establish the degree of environmental pollution induced by 1997 and 1998 printed circuit boards and the evolution of the hazardous pollutants with the technological development up to 2008. The printed circuit boards were submitted to a leaching test respecting the ratio L(liquid)/ S(solid) = 10 l/kg. The following parameters were measured: metals (As, Ba, Cd, Cr, Hg, Mo, Se, Cu, Ni, Pb, Sb, Zn), fluorides, chlorides, sulphates, phenol index, dissolved organic carbon, total dissolved substance, total organic carbon, polychlorinated biphenyls and petroleum products. Except Cu, Ni, Pb, Sb, Zn all the parameters were under the maximum values specified by the Council Decision of 19 December 2002 for accepting these printed circuit boards at landfills for inert waste. The

values obtained for Cu, Ni, Pb, Zn for 1997 and 1998 printed circuit boards are higher than the maximum values specified by the Council Decision of 19 December 2002 for accepting these printed circuit boards at landfills for inert waste. These values make them a potential danger for the environment when stored in open air and have the recommendation of storage at landfills for hazardous waste. The values for Cu, Ni, Pb, Zn for 2008 printed circuit boards are lower than the ones obtained for 1997 and 1998 printed circuit boards. Only Sb is increasing for 2008 printed circuit boards comparing to 1997 and 1998 printed circuit boards. According to this study, all 1997, 1998 and 2008 printed circuit boards can be deposit only at landfills for hazardous waste, their storage in open air being a real threat to the environment. 1997 and 1998 printed circuit boards present a high risk to pollute the environment with metals such as Cu, Ni, Pb, Zn then newer printed circuit boards such as those from 2008.

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Table 1. Leaching values for 1997, 1998 and 2008 printed circuit boards

No.	Determination	Unit	Sample code / Values						Limit Values*	Limit Values**
			1997_1	1997_2	1998_1	1998_2	2008_1	2008_2		
1.	Arsenic (As)	mg/kg	0.01	0.01	0.01	0.01	0.01	0.01	0.5	25
2.	Barium (Ba)	mg/kg	1.84	1.93	0.890	0.720	1.48	1.33	20	300
3.	Cadmium (Cd)	mg/kg	<0.01	<0.01	0.02	< 0.01	0.03	0.03	0.04	5
4.	Cromium (Cr)	mg/kg	0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.5	70
5.	Copper (Cu)	mg/kg	48.3	51.6	6.41	4.03	1.20	1.08	2	100
6.	Mercury (Hg)	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01	2
7.	Molibden (Mo)	mg/kg	0.01	0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.5	30
8.	Nickel (Ni)	mg/kg	0.73	0.75	1.02	1.55	2.58	2.41	0.4	40
9.	Lead (Pb)	mg/kg	8.44	8.71	26.9	34.0	0.56	0.34	0.5	50
10.	Antimony (Sb)	mg/kg	0.02	0.02	0.02	0.02	0.09	0.08	0.06	5
11.	Selenium (Se)	mg/kg	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.1	7
12.	Zinc (Zn)	mg/kg	21.4	23.6	11.0	8.79	7.35	6.98	4	200
13.	Fluorides(F^-)	mg/kg	< 0.5	< 0.5	0.6	0.6	< 0.5	< 0.5	10	500
14.	Chlorides (Cl^-)	mg/kg	4.86	5.35	7.9	15.0	5.35	4.76	800	25000
15.	Sulphates (SO_4^{2-})	mg/kg	7.03	7.45	11.0	9.86	6.15	5.88	1000	50000
16.	Phenol index	mg/kg	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	1	-
17.	DOC – Dissolved organic carbon	mg/kg	22	26	55	63	52	52	500	1000
18.	Total dissolved substance (TDS)	mg/kg	689	725	890	920	920	910	2500	100000

*Limit values according to COUNCIL DECISION of 19 December 2002 for waste acceptable at landfills for inert waste

** Limit values according to COUNCIL DECISION of 19 December 2002 for waste acceptable at landfills for hazardous waste

Table 2. Leaching values for organic content for 1997, 1998 and 2008 printed circuit boards

No.	Determination	Unit	Sample code / Values						Limit Values*	Limit Values**
			1997_1	1997_2	1998_1	1998_2	2008_1	2008_2		
1.	TOC – Total organic carbon	mg/kg	35	39	66	82	66	63	30000	6%
2.	PCB (polychlorinated biphenyls):	mg/kg								
	– PCB 28		< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	< 0.010	1	-
	– PCB 52		< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	1	-
	–PCB 101		< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	1	-
	– PCB 138		< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	1	-
	– PCB 153		0.017	0.017	< 0.011	< 0.011	< 0.011	< 0.011	1	-
	– PCB 180		0.019	0.021	< 0.011	< 0.011	< 0.011	< 0.011	1	-
	– PCB 194		< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	< 0.011	1	-
3.	Petroleum products	mg/kg	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	< 3.0	500	-

*Limit values according to COUNCIL DECISION of 19 December 2002 for waste acceptable at landfills for inert waste

** Limit values according to COUNCIL DECISION of 19 December 2002 for waste acceptable at landfills for hazardous waste

Figure 1. Mean values for Cu, Ni, Pb, Sb, Zn in case of 1997, 1998 and 2008 printed circuit board compared with limit values according to COUNCIL DECISION of 19 December 2002 for waste acceptable at landfills for inert waste