



Batch leaching tests of motherboards to assess environmental contamination by bromine, platinum group elements and other selected heavy metals



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HIGHLIGHTS

- Metals stripping from motherboards depend on the used leaching solution.
- Water, acetic acid, nitric acid and synthetic acid rain were used as leaching media.
- Heavy metals including PGEs were preferably leached with synthetic acid rain.
- Acetic acid solution dissolved the highest amounts of bromine.
- Motherboards should be considered as hazardous and treated prior to disposal.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, a batch leaching test was executed to evaluate the toxicity associated with chemicals contained in motherboards. The leaching solutions used were distilled water, nitric acid, acetic acid and synthetic acid rain solution. A total of 21 elements including Ag, As, Au, Br, Cd, Co, Cr, Cu, Hf, Ir, Mn, Ni, Os, Pb, Pd, Pt, Rh, Se, U and Zn were analyzed. In this study, the pH values of all the leachates fell within the range of 2.33–4.88. The highest concentrations of metals were obtained from the acid rain solution, whilst the maximum value of bromine was achieved with solution of acetic acid. Appreciable concentrations of platinum group elements were detected with concentrations around 3.45, 1.43, 1.21 and 22.19 $\mu\text{g L}^{-1}$ for Ir, Pd, Pt and Rh, respectively. The different leaching of the motherboards revealed the predominant presence of the toxic substances in the leached from the e-waste.

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1. Introduction

The global electronic waste (e-waste) production is assessed at 20–50 Mt per year (Robinson, 2009), equal to 1–3% of the estimated global urban waste production (1636 Mt) (Cobbing, 2008; OECD, 2008). Personal computers (PCs), cell phones and TVs contributed 5.7 Mt in 2010 and the estimates for 2015 amount to

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9.8 Mt (Widmer et al., 2005). Electronic computers with an average 3-year life cycle (Betts, 2008) contribute to the greatest extent to the total e-waste flow. Most e-waste is disposed in landfills, because effective reprocessing technology, which recovers the valuable materials with minimal environmental impact, is expensive (Robinson, 2009). According to Frazzoli et al. (2010), the most chemicals implicated in e-waste, are responsible of endocrine disruption and effects on the nervous and immune systems. Also, this hazardous components cause critical changes in pre-, postnatal stages of development of the most species. The PCs weigh from 8 to 14 kg; the two heaviest components are the housing and steel frame that constitutes 65–85% of the total weights of the PCs. The third largest components are the motherboards which account for 6–9%. However, this component should be treated as hazardous waste when being discarded because of the high concentration of heavy metals (Li et al., 2009a).

The implementation of the appropriate toxicity characteristic leaching procedure test (TCLP) (USEPA, 1999) has shown that e-waste discarded at urban waste dumping sites does not produce leachates with heavy metals concentrations exceeding the environmental limits established in Code of Federal Regulations, D-list (Spalvins et al., 2008). Nevertheless, this chemical cocktail generated from several electronic items was toxic for aquatic organisms (Dagan et al., 2007). Another factor to consider is that most components are metallic electronic waste and the leaching of pollutants begins with corrosion (Li et al., 2009b). TCLP is used to simulate the heavy metals leach from the PC components in the worst-case scenario in landfills. However, Jang and Townsend (2003) concluded that the amounts of heavy metals leached were much greater in the TCLP extraction fluid than in the landfill leachate, suggesting that the TCLP is over-conservative when used to estimate the leaching of heavy metals from e-waste in landfills. It could be because TCLP requires the samples to be crushed into particles of 9.5 mm; however, not all components could be reasonably sampled in such a small size. In this context, Li et al. (2009b) tested the leaching from heavy metals and argues that most e-waste components are metallic and the leaching of contaminants starts with corrosion and the 18 h^{-1} extraction in the TCLP test is not sufficient for the corrosion and leaching to complete.

Platinum group elements, known as PGEs (Pt, Pd, Rh, Ru, Ir and Os) can be naturally found only at very low concentration in the earth crust. These metals are predominantly used in automobile catalytic converters to reduce toxic exhaust fumes (Osterauer et al., 2011; Wiseman and Zereini, 2011). The PGEs are also used in electronic components because of their properties such as high melting points, high resistance to corrosion and low electrical resistance (Balcerzak, 2002). However, they have been associated with asthma, nausea, increased hair loss, increased spontaneous abortion, dermatitis and other serious health problems in humans (Pawlak et al., 2014). According to some experts, PGEs are mainly emitted in metallic form, and thus exhibit low toxicity. However, some of them are converted into soluble forms, which become bioavailable and begin to constitute a serious threat to animals and plants (Ravindra et al., 2004; Moldovan, 2007). The concentration of these metals has increased significantly in the last decades in diverse environmental matrices; like airborne particulate matter, soil, roadside dust and vegetation, river, coastal and oceanic environment (Merget and Rosner, 2001; Ek et al., 2004; Ravindra et al., 2004; Pawlak et al., 2014). The content of Pt in the tested food products from the Australian market varied and amounted to, e.g. $8.11\text{ }\mu\text{g kg}^{-1}$ in chicken liver and $0.13\text{ }\mu\text{g L}^{-1}$ in milk. Daily consumption of Pt was estimated at $1.73\text{ }\mu\text{g}$ for men and $1.15\text{ }\mu\text{g}$ for women (Pawlak et al., 2014). Hence, the determination of PGEs traces in environmental matrices requires a highly sensitive analytical methodology.

Bromine is another contaminant typically encountered in e-waste, which is likely the major source of bromine in the environment (Choi et al., 2009). The harmful effects of bromine on the body come from its interaction with iodine, which can lead to thyroid disease. Moreover, the bromine dumped in the environment has very negative health effects on daphnia, fish, lobsters and algae. Organobromine compounds are also damaging to mammals, especially when they accumulate in the bodies. The most important effects on animals are nerve damage and next to that deoxyribonucleic acid damage, which can also enhance the chances of development of cancer. Organobromine compounds are not very biodegradable; when they are decomposed inorganic bromines will consist. These can damage the nerve system when high doses are absorbed (Fu et al., 2011). In this context, primitive recycling of e-waste has become a global environmental problem introducing bromine and organic brominated compounds into soils and water resource.

There have been a number studies used to classify the hazards of e-waste by TCLP test, however, to our knowledge this is the first attempt of studying PGEs from electronic devices as potential pollutants of landfill. The main objective of this study was to examine the leaching of toxic PGMs and bromine from motherboards using different extraction fluids. This study will provide insight into how the PGMs and bromine from e-waste could pollute the landfills. Bromine, PGEs and fourteen heavy metal elements including Ag, As, Au, Cd, Co, Cr, Cu, Hf, Mn, Ni, Pb, Se, U and Zn were examined.

2. Sample treatment and methods

2.1. Sample preparation

Motherboards were tested for bromine and twenty metals without being reduced to a small size according to Li (2009). Four leaching solutions were used: distilled water (DW) had an initial pH of 4.8; nitric acid 0.1 M (NA) pH 3.68; acetic acid 0.5 M (AA) pH 4.20 and a synthetic acid rain solution (AR). This solution was prepared adding a percent mixture 60/40 weight of sulfuric acid and nitric acid to ultrapure water ($18.2\text{ M}\Omega\text{ cm}$) until the pH was 4.20 ± 0.05 . The motherboards were placed into polytetrafluoroethylene (PTFE) vessels within the different solution at a liquid-to-solid ratio of 20:1 on weight basis to evaluate the mobility of metals. The collected samples were filtered to determine the concentrations of the different elements. The total leaching period was 120 days.

2.2. Analysis of leachate

The total contents of fourteen heavy metals in the motherboards were determined using an ELAN DRC-e quadrupole ICP-MS instrument (Perkin Elmer SCIEX, Thornhill, Canada). An HF-resistant and high performance perfluoracetate (PFA) nebulizer model PFA-ST, coupled to a quartz cyclonic spray chamber with internal baffle and drain lines, cooled with the PC³ system from ESI (Omaha-NE, USA) was used.

For calibration purposes, six concentration levels were prepared and calibration curve were built for all elements. Each level of concentration was made in quintuplicate. The calibration curves were linear, with correlation coefficients with values above 0.995. The limit of detection (LOD) and the limit of quantification (LOQ), were calculated as the concentration of metals required to yield a concentration equal to 3.3 and 10 times the standard deviation of the blank records following IUPAC recommendations (Currie, 1999). The solutions used were acetic acid, distilled water, nitric acid and synthetic acid rain solution. The elements analyzed and their

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