SCREENING E-WASTE PLASTICS IN NIGERIA FOR BROMINATED FLAME RETARDANTS USING XRF – TOWARDS A METHODOLOGY FOR ASSESSING POPS PBDEs IN E-WASTE EXPORTS

Sindiku O¹, Babayemi J.O¹, Osibanjo O^{1,2}, Schlummer M³, Schluep M⁴, Weber R⁵

¹Department of Chemistry, Faculty of Science, University of Ibadan, Nigeria; ²Basel Convention Coordinating Centre for Training and Technology Transfer for the African Region, 1 Ijoma Road, University of Ibadan, Nigeria; ³Department Product Safety and Analysis, Fraunhofer-Institute for Process Engineering and Packaging, Giggenhauser Str. 35, 85354 Freising, Germany, ⁴Empa Technology and Society Lab, Lerchenfeldst.5, 9014 St. Gallen, Switzerland; ⁵5POPs Environmental Consulting, Ulmenstrasse 3, 73035 Göppingen, Germany

Introduction

Pentabromodiphenyl ether (PentaBDE)^A and certain congeners of octabromodiphenyl ethers^A (OctaBDE) were added to Annex A of the Stockholm Convention (05/2009)^{1,2}. Therefore the listed PBDEs (POPs PBDEs) are officially recognised as persistent organic pollutants (POPs) under the Stockholm Convention which prohibits production, use, import, and export with some defined exemptions. Furthermore Article 6 of the Convention requires that wastes containing POPs has to be managed in a manner protective of human health and the environment³. The new listing therefore requires parties of the Stockholm Convention to take appropriate measures to reduce or eliminate releases of POPs PBDE^A from stockpiles and wastes. The listing of PBDEs, unlike the original Stockholm POPs, includes specific exemptions allowing for recycling and the use in articles of recycled materials containing these chemicals. This possibility to include POPs in recycled products lead to exposure in the recycling stage (and future recycling cycles) and in use of recycled products generating new health and environmental risks^{4,5}.

The Conference of the Parties decided to undertake a work programme to provide guidance to parties on how best to restrict and eliminate brominated diphenyl ethers and the other newly listed chemicals and a technical paper has been prepared in this respect^{4,5}. Furthermore recommendations have been developed from the POPs Reviewing Committee for the Stockholm Convention Conference of Parties⁶.

The challenge is now how to practically control PBDE in products and the recycling flows. This is in particular a problem for developing/economy in transition countries where state of the art recycling plants with monitoring capacity do not exist and measurement capacity is not established. These countries lack appropriate destruction facilities which leads to open burning or dumping of such hazardous wastes causing environmental pollution⁷⁻⁹.

Plastic in electronic waste (e-waste) is considered to contain the largest share of POP PBDE in the waste stream followed by polyurethane foam in car/transport, mattresses or construction. While for many years the largest amount of e-waste exported from the US and Europe was mainly shipped to China, African countries such as Nigeria were receiving large volumes since some time as well.^{10,11} In addition those countries are generating in increasing amount of their own e-waste.¹² While the main incentive for e-waste recycling is the recovery of precious and other metals, increasing oil prices mean that plastic is also increasingly recycled. Nigeria has already developed some plastic recycling activities and currently the government is planning to develop more than 20 plastic recycling facilities. In this instance it needs to be assured that hazardous chemicals like POPs, PBDE or heavy metals are controlled and phased out where feasible and do not end up in sensitive recycled plastic products like children toys or household goods.

The objective of this study is a screening of brominated flame retardants in plastic from TV sets and computer monitors (containing the main plastic share of electronics) present in Nigeria. In this paper the sample selection and the assessment of the presence of flame retardants by a screening technology (XRF) for pre-screening of the samples is presented. This approach can be used in practice for separation of BFR and non-BFR plastic. The study is a part of a project to establish guidance for the sampling and assessment of POPs PBDE in electronics for the Stockholm Convention.

^A The listing of POPs PBDEs include tetrabromodiphenyl ethers, pentabromodiphenyl ethers, hexabromodiphenyl ethers and heptabromodiphenyl ether. The octabromodiphenyl ether homologue, nonabromodiphenyl ethers and the decabromodiphenyl lether are not listed as POP. However the debromination of these highly brominated diphenyl ethers lead to the formation and release of POPs PBDEs.

Materials and methods

Samples of plastics from electronics (plastic casings from TV sets and computer monitors) were taken from eight locations in Ogun state and Lagos state in south west Nigeria. The sampling was carried out between January 31 and March 16, 2011.

Elemental analysis by EDXRF: Samples were screened by EDXRF on a SPECTRO X-LAB 2000 (Spectro, Germany) using the general calibration of the instrument. In addition to bromine and chlorine also heavy metals were included in the screening. With respect to single housing materials, squares with 40 mm X 40 mm dimension were cut out of the housings and analysed without further pre-treatment.

Results and discussion

1. Selection of samples and sample preparation

In this first sampling campaign of plastics entering and present in Nigeria, TV sets and computers were targeted. These two electronic groups contain the largest share of plastic in e-waste. Furthermore the recycling of the plastic of these e-products is of particular interest from an economic perspective.

Samples were selected from the districts Oke-Ilewo, Ago-Oba, Ago-Oba-Lafenwa, Panseke, Sokori and Sapon, all in Abeokuta and Benja Villa in Ota in Ogun state; and the Computer Village in Lagos. The samples were specifically selected from waste storages, electronics workshops, roadsides, dumpsites and dismantling sites. They were of different sizes, shapes and colours. The labels on the TVs and computer monitor plastic housings were examined for information on the manufacturer, brand, model, serial number, year and origin of production. Mainly for TV samples, the year of production were found printed on the inside of the plastic casings. The information was immediately recorded and about 250 cm² sizes were cut from each sample. Dismantling and cutting were done with simple tools (Figure 1). A hole was made on the cut samples through which a metal tag (Figure 2) was attached with the aid of a safety pin (Figure 3). These were transferred to the workshop where 40 mm X 40 mm squares were cut (Figure 4), and the cut squares packaged in labeled drug envelops (Figure 5).

The ranges of the year of production were 1987-2006 for computers, and 1981-2004 for TVs. This time span is considered being the most relevant for the use of POPs PBDE as their use is thought to have been stopped in about 2004. The numbers of samples with the regions of origin (production or assembly) are shown in Table 1. A total of 382 samples were collected - 224 from Computers and 158 from TV sets. For computer samples, the highest proportion was from Asia (100), followed by America (74), and then Europe (50). Most of the TV samples were obtained for Europe (100), followed by Asia (58), and none from America. This broadly reflects presence of these e-wastes in Nigeria. Second hand TVs are not imported from the US as the systems are not compatible.



Figure 1: Sampling tools

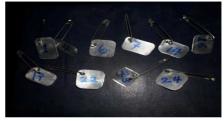


Figure 2: Labelling tags

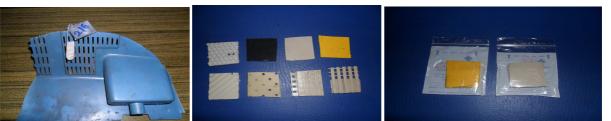


Figure 3: Labeled field samples

Figure 4: Cut squares

Figure 5: packaged samples

Region	Computer	TVs	Total	
Europe	50	100	150	
Asia	100	58	158	
America	74	0	74	
Total	224	158	382	

 Table 1: Number of samples from each region of production/assembly

2. Results of XRF screening

EDXRF analysis was performed in order to identify chlorine and bromine as indicators for brominated and chlorinated flame retardant systems. Also phosphorous was measured to indicate the phosphor based flame retardants. The XRF analysis also allows the screening of heavy metals. Antimony (Sb), lead (Pb) and cadmium (Cd) as potentially relevant heavy metals for further interpretation and contamination assessment were analysed. At the time of compilation of this abstract about 220 samples from the 382 samples have been analysed by XRF.

Content of brominated and other flame retardants in computers and TV sets from the three regions (Figure 6) From the computers from the US (currently analysed n=30) about 60% were fully brominated flame retarded (Bromine content in the plastics from 5 to 11%). From the computers from Asia (currently analysed n=50) 70% were found to be fully brominated flame retarded (bromine content 4.7 to 9.8%). From the computers assembled/produced in Europe (currently analysed n=28) 43% were found to be fully brominated flame retarded (bromine content between 5.4 to 7%).

32 of the currently screened 108 computer casings contained phosphor at a level between 0.5 to 2.4% indicating that about 30% of these samples were equipped with phosphor organic flame retardants (PFR).

Only 6.5% of computer monitor casings did not contain flame retardant systems based on BFRs or PFRs.

A range of plastic samples from computers and TV sets contained bromine levels at a concentration between 100 ppm and 10000 ppm (Figure 6). This bromine content is not sufficient to function as flame.retardant and was probably not specifically added for this purpose. Most probably the BFRs stem in these samples from recycling of partly BFR containing plastic.

From the currently screened plastic casing from TV sets from Europe (n=100) about 36% were fully flame retarded with BFRs (2.2 to 9.2% of bromine). 5 of the TV sets had phosphor levels of 0.5 to 1% indicating the use of PFRs for these sets.

From the plastic casing from TV sets from Asia (n=20) only 3 (15%) were fully flame retarded with BFRs (6 to 8.2% of bromine). Phosphor levels were low in all 20 samples showing that the screened TV casing from Asia have not been treated with phosphorus flame retardants.

As mentioned above TV sets from the US are not imported as second hand systems since the systems used in US and Nigeria are not compatible.

A large amount of TVs (>60%) did not have either BFR or PFRs. From the current screening it can not be concluded if the plastic from these TV sets were not flame retarded at all or of other means of flame retarding (other plastic type or certain inorganic flame retardants) have been used.

Overall, a very high percentage of the sampled computer monitoring cases present as electronic wastes in stores and workshops in Nigeria contain brominated flame retardants.

With the current analysed data it appears that computers assembled/produced in Europe contain a lower percentage of brominated flame retardants in the casings. The reason for this is probably the lower flammability standard required in Europe.

The share of television casings fully flame retarded with BFRs were somewhat lower (average about 30%) compared to computers.

As mentioned in the introduction, one final aim of this project is the assessment of POPs PBDE in electronic waste in Nigeria. The XRF screening can only establish the presence of brominated/chlorinated compounds and not whether POPs PBDE are present. However, after this first screening about 40% of the sampled electronics can be excluded from the further detailed analysis of PBDE (and other brominated flame retardants).

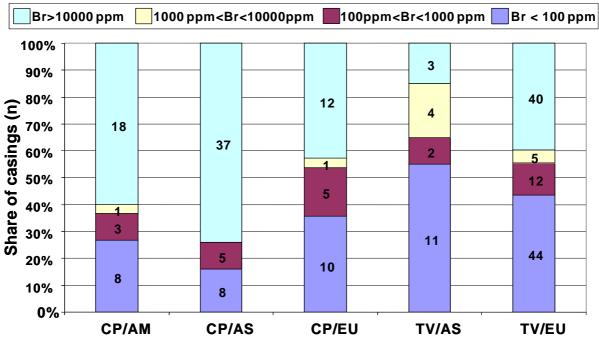


Figure 6. Bromine content in sampled TV sets (TV) and computers monitors (CP) produced/assembled in North America (AM), Asia (AS) and Europe (EU).

Acknowledgements

The fund from the Norwegian government to the Stockholm Convention Secretariat for financing this project is appreciated.

References

- 1. Stockholm Convention (2009a). UNEP/POPS/COP.4/SC-4/14 Listing of hexabromodiphenyl ether and heptabromodiphenyl ether.
- 2. Stockholm Convention (2009b). UNEP/POPS/COP.4/SC-4/18 Listing of tetrabromodiphenyl ether and pentabromodiphenyl ether.
- 3. Stockholm Convention (2001). Stockholm Convention on Persistent Organic Pollutants (http://www.pops.int/documents/convtext/convtext_en.pdf.)
- 4. Stockholm Convention (2010). Technical Review of the Implications of Recycling Commercial Pentabromodiphenyl Ether and Commercial Octabromodiphenyl Ether. 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/2)
- 5. Stockholm Convention (2010). Technical Review of the Implications of Recycling Commercial Pentabromodiphenyl Ether and Commercial Octabromodiphenyl Ether. 6th POP Reviewing Committee meeting (UNEP/POPS/POPRC.6/INF/6)
- Stockholm Convention (2011) Work programmes on new persistent organic pollutants. 5th Conference of Parties meeting. UNEP/POPS/COP5/15
- 7. Wong MH, Wu SC, Deng WJ, Yu XZ, Luo Q, Leung AO, et al. (2007) Environ Pollut.149: 131-40
- Sepúlveda A, Schluep M, Renaud FG, Streicher M, Kuehr R, Hagelüken C, Gerecke AC (2010); Environmental Impact Assessment Review 30: 28–41
- 9. Weber R, Watson A, Forter M, Oliaei F. (2011); Waste Management & Research 29 (1): 107-121
- 10. Nnorom IC, Osibanjo O (2008); Resources, Conservation and Recycling 52: 1362–1372
- 11. Nnorom IC, Osibanjo O (2008); Waste Management 28: 1472-1479
- 12. UNEP (2009) Recycling from e-waste to resources. July 2009