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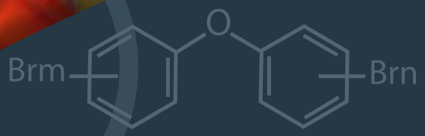
MANUAL ON TECHNIQUES AND METHODS FOR IDENTIFICATION AND SEPARATION OF WASTE CONTAINING POLYBROMINATED DIPHENYL ETHERS (PBDEs) INTENDED FOR E-WASTE RECYCLERS



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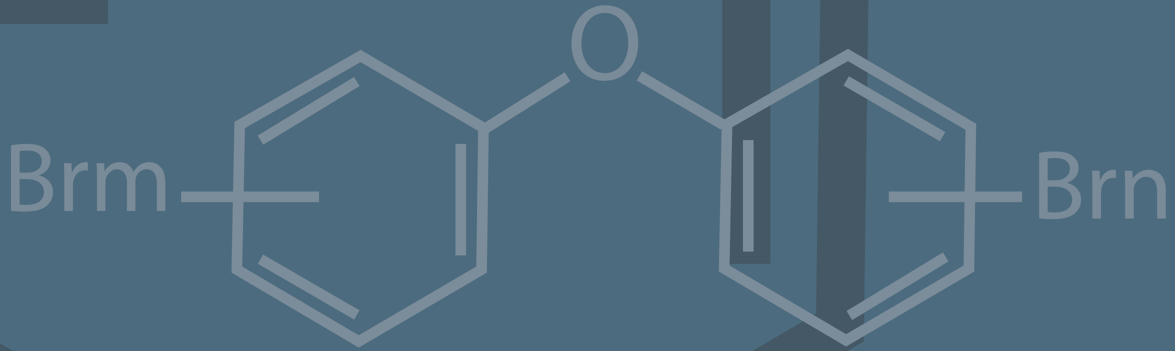
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MANUAL ON TECHNIQUES AND METHODS FOR IDENTIFICATION AND SEPARATION OF WASTE CONTAINING POLYBRONATED DYPHENIL ETHERS (PBDEs) INTENDED FOR E-WASTE RECYCLES

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Contents

INTRODUCTION

This document - Manual on techniques and methods for identification and separation of waste containing polybrominated diphenyl ethers (PBDEs) was prepared for e-waste recyclers in order to assist waste operators in identifying and separating an e-waste that contains PBDEs. This document was prepared by national expert within UNEP/UNDP BRSM Synergy project in Serbia according to *The revised guidance on best available techniques and best environmental practices for the recycling and waste disposal of articles containing polybrominated diphenyl ethers listed under the Stockholm Convention* and in line with technical infrastructure of our domestic e-waste operation.

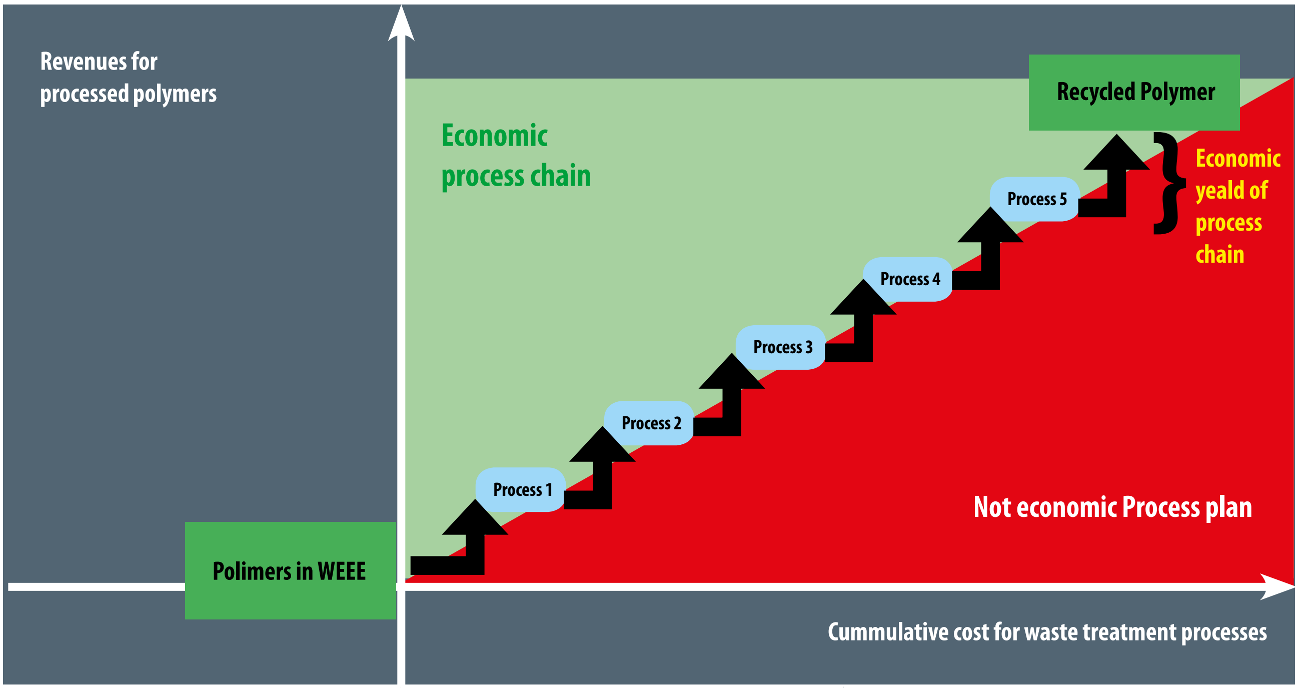
1. METHODS OF SEPARATION OF POLYMERS CONTAINING POP – PBDEs

Separation technologies are designed to pick POP-PBDE-free plastics out of WEEE plastics with the aim of recovering valuable and marketable products, the sale of which generates much of the process revenues. Thus, development and management and combining these technologies is driven mainly by economy of the overall process chain. That means that separation of POP-PBDEs is only a part of the overall strategy to produce valuable products with reasonably high yield and quality accepted by producers of new products (see Figure 1).

WEEE plastics may be transformed into valuable plastic for recycling by a chain of optimized processes sometimes performed by more than one company. The process is only economically feasible if the cumulative cost of processing is lower than the revenues for the recycled product (see Figure 1). Therefore, separation of POP-PBDE-containing plastic needs to be effectively integrated with the main driving forces of a recycling plant: the technologies used for shredding of WEEE and separation of polymers for polymer material recycling and for metal recycling.

The following techniques could be used at a plant recycling plastics from WEEE as BAT/BEP:

- Manual dismantling approaches or shredding technologies;
- Sorting technologies to separate possibly POP-PBDE-containing bulk and shredded plastics;
- Combination of technologies for optimization of the separation process;
- Full-scale plants to separate WEEE and POP-PBDE-containing plastics.



Possible processes	Separation principle	Capable to remove or eliminate BFR
Manual XRF	X-ray fluorescence	Yes
Manual NIR / MIR	Polymer seperation basing on IR spectra	Not those regulated by RoHS and Stockholm Convention
Manual sorting	Knowledge and polymer labeling	(Yes)
Grinding and removal of foreign materials	Magnetic and eddy current seperation	No
Airstreem sorting	Specific weight	No
Sink and float	Density	Yes
NIR sorting	Polymer seperation basing on NIR spectra	Not those regulated by RoHS and Stockholm Convention
Laser sorting	Polymer seperation basing on laser spectroscopy	Not approved yet
XRT	X-ray transmission	Yes
Compounding and melt filtration	Sieving	No
Upgrade	Addition of additives	No

Figure 1. *Stepwise separation of polymers from waste of electrical and electronic equipment and their transformation into valuable plastic-for-recycling.*

There are no strict rules for the choice of processes; however, for the purpose of this guidance at least one principle of POP-PBDE removal should be applied. In addition to that, the processes may be performed by more than one company.

1.1. MANUAL DISMANTLING APPROACHES

Recycling companies handling CRT (Cathode Ray Tube) monitor housings often manage these plastics separately, based on their experience of the specific type of polymers and type of flame retardant, thus keeping these streams "cleaner". Colours of plastics could influence the effectiveness and efficiency of the sorting technologies engaged after sorting processes; therefore it is important to separate plastics into different colours considering, in particular, challenges with separation of black/dark plastic materials.

BEP approach applied in Sweden

Retegan et al. (2010) describe the current principal method used in the Swedish recycling industry for the separation of plastics from TVs and computer monitors containing POP-PBDEs. This approach is used only for TVs and monitors; however, it is not clear how many of the non-marked plastics do contain POP-PBDEs. The listed items are removed manually from the waste stream. Training and experience in manually sorting WEEE plastics and parts containing POP-PBDEs is needed to effectively sort polymers and remove those components. Even experienced manual sorting operatives cannot, however, determine which types of POP-PBDE are incorporated in the polymers. Thus, the report recommends that manual sorting be supervised by spot-checks using XRF measurements. Although this report does not include information on the effectiveness of this approach, it claims that, for waste TV and PC monitors, the accuracy of these sorting methods is satisfactory for complying with European directives/legislation.

The compliance with legislation is not surprising as the number of residual articles still containing PBDEs has now dropped to low levels in Europe *(Wäger et al., 2010).*

A similar situation could be expected in the Republic of Serbia, taking into account that the national legislation in this area is harmonized with the EU and that most of the e-equipments are imported from the EU member states, with the regulatory ban on the import of used (second hand) computer equipments being in place in our country. Also, it should be emphasized that it is possible that the percentage of e-waste that contains PBDEs in our country is slightly higher than in the EU, taking into acount that the average time of use of e-equipment in our country is longer than in the EU because of the socio-economic reasons.

1.2. XRF SEPARATION TECHNOLOGY

WEEE may contain components that originate from previous recycling of POP-PBDE-containing polymers. These may contain mixtures of different BFRs, including c-OctaBDE, but exhibit bromine levels in the range of 100-1000 ppm *(Bantelmann et al., 2010; Chen et al., 2009, 2010; Sindiku et al., 2011)*. XRF is sensitive enough to trace these materials, detecting the total bromine content. It can be used for detection and separation of POP-PBDE-containing plastic with a bromine detection limit of 10 to 100 ppm.

It is important to note that in accordance with the provisions of the Law on Chemicals and the Rulebook on Restrictions and Prohibitions on the Production, Marketing and Use of Chemicals (harmonized with EU POPs Regulation), the production, placing on the market and use of new articles containing PBDEs is allowed in concentrations below 0,001 %. Additionally, if a new product is produced from recycled plastics, it is allowed to produce, market and use mixtures and products which are fully or partially produced from recycled materials or waste ready for new use, provided that they contain polybrominated diphenyl ethers in concentrations lower than 1000 ppm.

The time requirement for a measurement when using manual devices is only a few seconds. With a cost of approximately US$20,000 to US$50,000, its use in small size enterprises may be limited. Additional costs for software is about US$ 3,000. Since the manual XRF instrument needs a direct contact to the material surface, it is not applicable for use in automated sorting systems but is used in the dismantling stage. Coated materials need to be specifically addressed by scratching the coating.

The XRF technology is applied for instance by Austrian dismantlers since the Austrian Waste Treatment Obligation Ordinance requires the monitoring of plastics from WEEE if plastic wastes are subject to material recycling *(Aldrian et al. 2014)*. The limit value of 800 mg bromine /kg d.s. is set in the Ordinance which correlates with a limit of 1000 mg of the sum of PBDE/kg d.s. and is based on the worst case assumption that all the detected bromine is due to PBDEs. A large-scale study to determine the levels of PBBs and PBDEs in visual display units concluded that about 15% of plastic waste from TV casings and about 47% of plastic waste from PC-CRT casings show significantly higher levels of PBDEs than 0.1% *(Aldrian et al. 2014)*. In a similar screening study in Nigeria, 32.9% of the sampled TV CRT and 66.1% of computer CRT casings contained bromine at a concentration above 1% considered to be flame retarded with BFRs with average plastic also exceeding 0.1% POP-PBDEs *(Sindiku et al. 2014)*.

According to the Austrian study, manual XRF detector was proven as an effective tool and allows fast monitoring of large volumes of waste plastics in a limited period of time. Manual XRF detectors are a quite expensive acquisition, but the maintenance costs are manageable. The use of stationary XRF requires some measures of reconstruction in order to comply with radiation protection requirements and is therefore much more expensive.

1.3. SEPARATION OF POLYMERS BY SINK AND FLOAT TECHNOLOGIES

Polymer types exhibit different specific weights, and therefore liquid media with appropriate densities allow for separation of different thermoplastics into density groups. The salinity, and hence the density, of the liquid media can be changed by adding different salts. If water is being used, for example, the density can be raised for 15% by adding the magnesium sulphate. BFR additives increase the density of the ABS and HIPS materials significantly, when added at typical concentrations (> 3%). If treated in an appropriate liquid medium, bromine-free polystyrene will float while bromine-containing polystyrene will sink, thus separating the polymers containing bromine from other polymers *(Schlummer and Maeurer, 2006)*.

A simple two-stage separation has recently been tested successfully in a German collaborative project (SpectroDense; InnoNet, 2009). At first, the mixture is treated in a liquid with a density of around 1,100 kg/m^3. The float fraction will mainly consist of PP, PE and BFR free PS, and ABS; whereas BFR-containing, but also PPO/PS and PC/ABS (both flame retarded with phosphate based FR) and highly filled PP items will sink. The float fraction is further treated with water (density 1,000 kg/m^3) to separate HIPS and ABS from PP and PE.[1]

Valuable polymers as PC/ABS and PPO/PS (normally free of POP-PBDEs) could be separated from the heavy fraction by downstream NIR techniques, as these materials are grey in many cases.

For the selected input fractions, the sink and float technology products are very clean and qualitatively good in respect to separation of BFR-containing materials. TV housings are mostly made of HIPS.

Since that about 30%[2] of the casings in Europe contain BFR, sink and float (S/F) is a good way to separate them, and the high yields of BFR free materials suggest a high cost-efficiency of the process *(Schlummer, 2011)*. In Africa, this share seems higher *(Sindiku et al., 2009)*.

With respect to BFRs, and especially POP-PBDEs, S/F has been reported to effectively separate BFR-containing materials from non-BFR types of ABS and/or HIPS *(Schlummer and Maeurer, 2006)*. It has been reported that the S/F has been used in separation of BFR rich fractions of TV/PC from low BFR fraction intended for recycling purposes in Sweden *(Retegan et al., 2010)*.

One of the challenges of the S/F technology is to develop separation technologies for fractions of HIPS / PPO (1.150 kg/m^3) and PC/ABS (1.180 kg/m^3) due to presence of phosphorus-based fire retardants (see below).

With respect to plastics from small electronic equipment and mixed WEEE plastic from recycling, S/F can produce almost bromine-free plastic fractions, consisting largely of ABS, PS (incl. HIPS) and polyolefins. Due to a large share of black plastics in these low-bromine fractions, which inhibit a downstream NIR separation, it is challenging to produce high quality polymers with a good market price as useful output. Currently, the yield of these techniques does not normally allow economic recovery of polymers. Therefore, unless the bromine-free fraction can be converted into valuable plastic for recycling, S/F is unlikely to be widely used. Operators are (understandably) unwilling to use a separation technique to produce what might be in fact two new waste streams without adding value to the output *(Schlummer, 2011)*.

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[1] These two binary mixtures could further be separated by NIR or electrostatic separation.

[2] The content of BFR will depend on the region and the legislation for flammability standards - in the United States/Canada most of the casings contain flame retardants.

1.4. COMBINATIONS OF TECHNOLOGIES FOR PRODUCING MARKETABLE PRODUCTS

None of the individual techniques described above have the ability to separate mixed plastic from WEEE: to ensure that the plastic is separated into marketable polymer fractions and that, at the same time, POP-PBDE/BFR-containing plastics are separated. Therefore, combinations of the techniques need to be used in practice.

In addition, no technique achieves a 100% separation, leading to residual POP-PBDE levels in the intended bromine-free fraction. In the case of handheld sorting this is due to errors by the operatives. For automated systems, the sorting efficiency with blowing bars has its limits and the purity of sorted fractions is normally below 95%. This section describes process chains, which include steps suitable (in principle) for the separation of POP-PBDEs/BFRs followed by technologies focusing on polymer separation and upgrade of fractions (whereas section 4.3.5 lists existing plants). The process combinations are based only on technical considerations and do not take into account the economic feasibility, which may vary significantly in different countries. Local costs and revenues therefore need to be calculated for the different combinations of technologies.

Dismantling→ NIR →Sink and float→Electrostatic separation

Dismantling sites usually recover CRT glass from computer monitors. As these products contain rather large plastic housings, which are in most cases built by PS, ABS or blends of these polymers with polycarbonate (PC/ABS) or polyphenylene oxide (PPO/PS), dismantling personnel can easily produce a polymer fraction from these items upon the established glass recycling process.

After a coarse crashing process, the waste plastics material can be separated into the following polymer fractions by online NIR: light PS, light ABS, light PC/ABS, light PP, light PPO/PS and dark materials that cannot be identified with NIR.

The light PS and light ABS, as well as the dark fraction, are most likely containing higher amounts of BFR, which can be separated by the sink and float technology when performing two separation runs in density media of 1,000 and around 1,100 kg/m^3. The sink and float technology is based on the fact that BFR rich ABS and PS exhibit significantly higher densities compared to non-BFR ABS and PS.

As the dark density fraction 1,000-1,100 kg/m^3 is intended to contain both ABS and PS, a subsequent separation of both materials is preferred and can be performed by electrostatic separation. The latter technique is available on an industrial scale and works best for binary and well dried plastic mixtures. In this process, the plastic mixture is fed via a vibrating conveyor into a so-called tribo-electric charging unit. Different plastics are charged here selectively and specifically according to the material, taking on a positive or negative charge. After the charging has taken place, the plastic mixture reaches a high tension field where the components are separated electrostatically into pure sorted fractions according to their charges: positive particles are attracted by a negative electrode, while negative particles are rejected and vice versa.

Dismantling →Sink and float →Electrostatic separation

Dismantling sites usually recover CRT glass from TV sets. As TVs typically include large plastic housings predominately composed of PS and only rarely by ABS or PP, dismantling personnel can easily produce a polymer fraction from these items to supplement the established glass recycling. Recent research has shown that it is possible to reduce the amount of non-BFR-ABS in this fraction to a minimum by appropriate training. This is important, since TVs contain dark plastics unsuitable for NIR sorting. After a grinding process, the PS rich fraction is separated in a BFR rich and almost BFR free fraction by S/F. As the dark density fraction 1,000-1,100 kg/m^3 contains both ABS and PS, a subsequent separation of both materials is preferred and can be performed by electrostatic separation. The latter technique is available on an industrial scale and works best for binary and well dried plastic mixtures *(Hamos, 2012; Wersag, 2012; see table 2)*.

Dismantling→ Manual sorting →Sink and float

The most elaborative approach is manual sorting, preferably assisted by handheld NIR and a handheld bromine identification tool (SSS or XRF). In addition to these tools, sorting personnel should check casing for material stamps indicating the type of material. By using these techniques, trained personnel may be able to collect a high share of (almost) BFR free materials from plastic streams. Subsequently, NIR technologies will enable production of fractions of defined polymer types for further processing. The disadvantage of this approach may be that large items like housing of printers, monitors and TVs with high levels of BFRs are side products requiring a sound waste treatment. In contrast, plastic parts made from non-BFR or low BFR equipment are normally smaller and not often dismantled and treated by shredder techniques.

Shredder → Sink and float → Electrostatic separation

Shredded plastics from mixed WEEE (especially small WEEE appliances) have to pass removal steps for FE and non Fe metals and dust before they may be treated by a two-step sink and float process in density media of around 1,100 kg/m^3 and 1,000 kg/m^3. The fraction smaller than 1,000 kg/m^3 is intended to be rich in PP and minor amounts of PE. The intermediate density fraction is considered to contain BFR free ABS and PS as well as filled PP types. These three fractions may be subsequently separated by electrostatic separation (Hamos, 2012; Wersag, 2012; see table 2).

Shredder →XRT →Spectroscopy

From mixed WEEE fraction, a plastic fraction is recovered in state of the art WEEE treatment plants by a set of smashing, grinding and mechanical separation processes. Since this fraction has a typical particle size below 20 mm, automated online rather than manual separation processes are required for further upgrading this fraction for polymer recovery.

Bromine and chlorine may be removed by online XRT technology producing a low-bromine fraction of mixed plastics composed of up to 16 polymer types. The main polymer types (PS, ABS, and PP) may be recovered subsequently by online NIR, however, this technique is limited to the fraction of light materials, which is unfortunately not the major fraction of WEE plastics.

Under the current pilot test, Fraunhofer IVV (Freising, Germany) and Unisensor (Karlsruhe, Germany) are testing and optimizing a new automated sorting technique based on laser spectroscopy. Results obtained so far clearly indicate that this technique is able to separate several polymer types out of a mixed input stream of shredded plastics automatically with high throughput rates (~1 ton per hour). Laser spectroscopy (in contrast to NIR) can identify black and dark plastics and might therefore become a key technology to transform BFR free plastic shred from WEEE into marketable sorted polymer type fractions. Further investigations are focusing on the identification of BFRs with laser spectroscopy applying comparable high throughput rates. *(Schlummer, 2011; Unisensor, 2012).*

2. COMPARISON OF TECHNOLOGIES TO SEPARATE POLYMER STREAMS

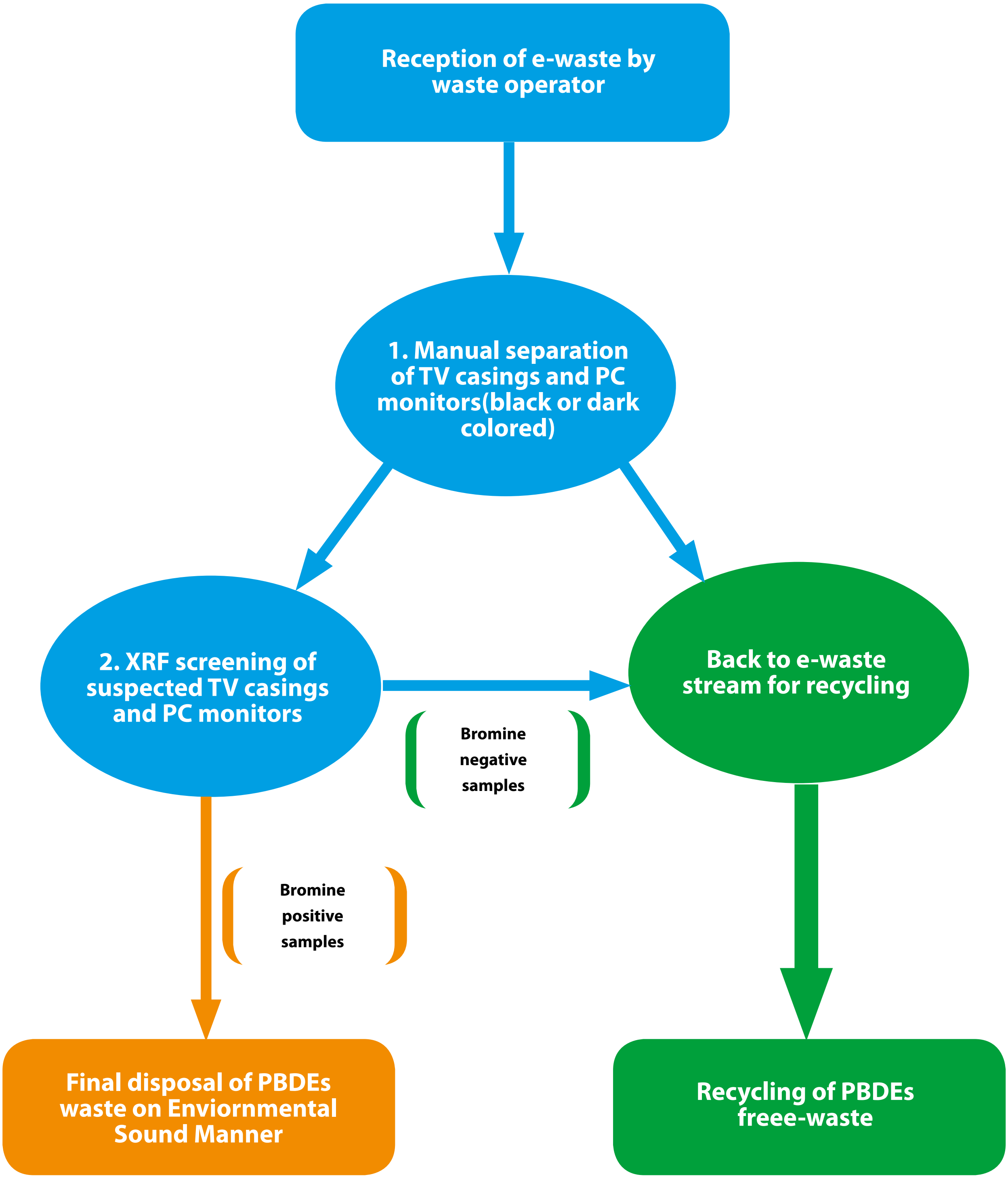
Some practical combinations of technologies used for separation of polymers for different input materials are listed in table 2. Also the possible product output, the status of development and the economy or available commercial systems are mentioned.

Table 2: *Combinations of separation techniques, input materials, products, status of development and remarks on related economy*

Combination	Suitable input	BFR free products	Status of development	Economy	Reference
Dismantling → NIR → sinkand float → Electrostatic separation	Plastics from dismantled WEEE items	ABS, PS	Approved	Economy depends on the yield of BFR free products	Schlummer (2011)
Dismantling → Sink and float → Electrostatic separation)	TV casings	HIPS	Approved	Approved	Schlummer (2011)
Dismantling → manual sorting (→ sink and float)	Plastics from dismantled WEEE items	ABS, PS, PC-ABS	Approved	Not approved in industrial countries	
Shredder → Sink and float → Electrostatic separation	Mixed WEEE (small appliances)	ABS, PS, PP	Approved	System runs successfully at wersag AG (Großschirma, Germany)	Hamos (2012) Wersag GmbH (2012)
Shredder → XRT → spectroscopy	Mixed WEEE	BFR and PVC "free"	Approved	No information	Schlummer (2011) Unisensor (2012)

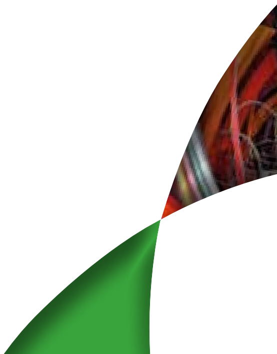
ANNEX

Schematic overview of the optimal procedure for identification and separation of plastics potentially containing PBDE from e-waste



Abbreviations and acronyms

ABS	Acrylonitrile-Butadiene-Styrene
ASR	Automotive Shredder Residue
BAT	Best Available Techniques
BDP	Bisphenol A-bis(diphenylphosphate)
BEP	Best Environmental Practices
BFR	Brominated Flame Retardant
BSEF	Bromine Science and Environmental Forum
c-DecaBDE	Decabromodiphenyl Ether
c-OctaBDE	Commercial Octabromodiphenyl Ether
c-PentaBDE	Commercial Pentabromodiphenyl Ether
CFC	Chlorofluorocarbon
CKD	Cement Kiln Dust
COP	Conference of the Parties
CRT	Cathode Ray Tube
DOPO	Dihydrooxaphosphaphenanthrene
EAF	Electric Arc Furnace
EEE	Electrical and Electronic Equipment
ELV	End-of-life Vehicle
EMS	Environmental Management System
ESM	Environmentally Sound Management
FPF	Flexible Polyurethane Foam
FR	Flame Retardant
GHG	Greenhouse Gas
HBB	Hexabromobiphenyl
HBCD	Hexabromocyclododecane
HFC	Hydrofluorocarbon
HIPS	High Impact Polystyrene
MSW	Municipal Solid Waste
NIR	Near-Infrared
ODS	Ozone Depleting Substances
PBB	Polybrominated Biphenyl
PBDE	Polybrominated Diphenyl Ether
PBDD/PBDF	Polybrominated Dibenzo-p-dioxins and Polybrominated Dibenzofurans
PBT	Polybutylene Terephthalate

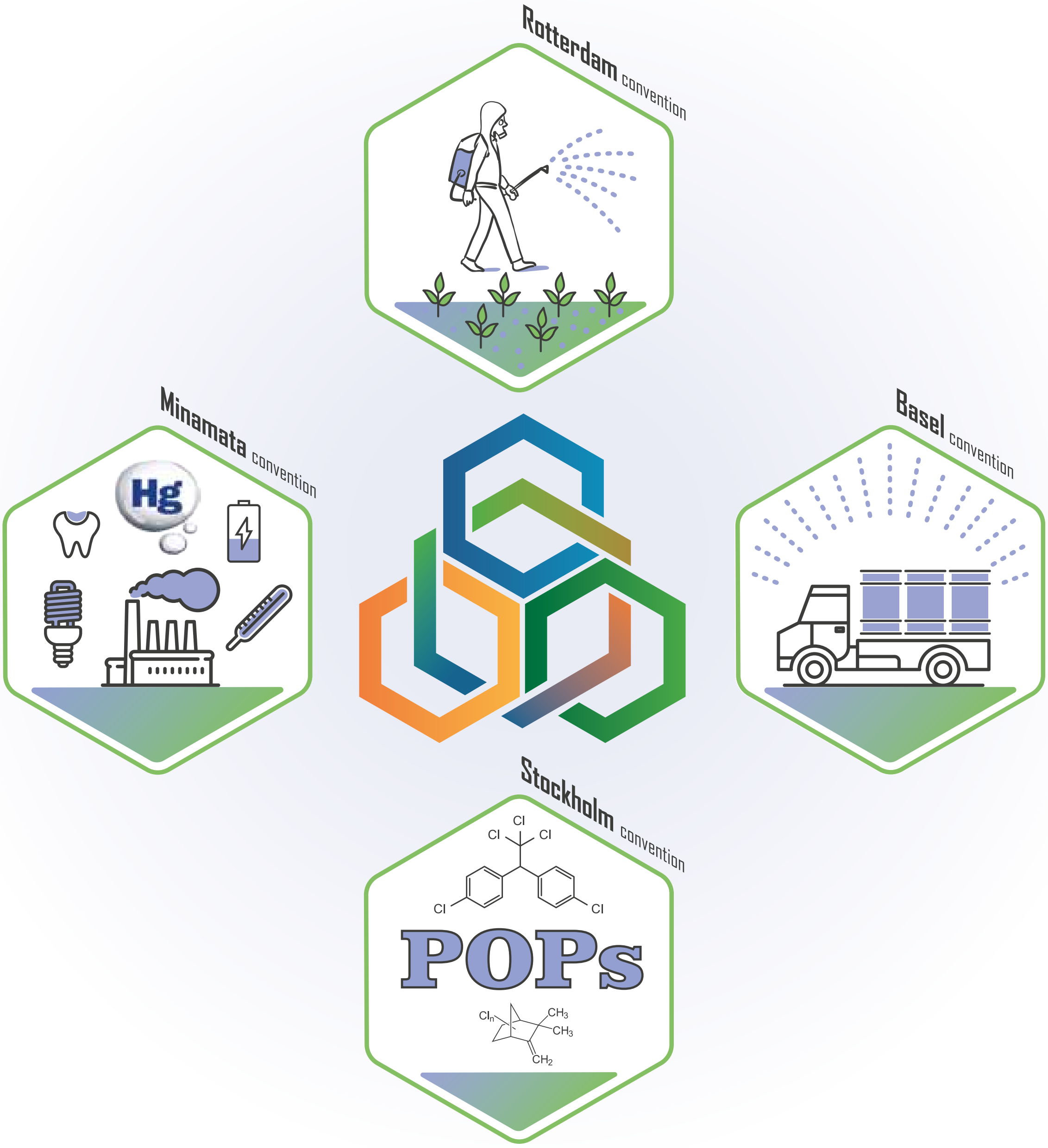


PC	Polycarbonate
PCB	Polychlorinated Biphenyl
PCDD/PCDF	Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans
PET	Polyethylene Terephthalate
PFR	Phosphorous Based Flame Retardant
POPs	Persistent Organic Pollutants
POPRC	Persistent Organic Pollutants Review Committee
PP	Polypropylene
PPE	Polyphenyl Ether PPO Polyphenylenoxide
PS	Polystyrene
PUR	Polyurethane
PVC	Polyvinylchloride
PWB	Printed Wiring Board
PXDD/PXDF	Polybrominated Polychlorinated Dibenzo-p-dioxins and Dibenzofurans
RDP	Resorcinol-bis (Diphenylphosphate)
RoHS	Restriction of the use of certain hazardous substances in electrical and electronic equipment
S/F	Sink and Float
SVOC	Semi-volatile Organic Compound
VOC	Volatile Organic Compound
WEEE	Waste Electrical and Electronic Equipment
XRF	X-ray Fluorescence
XRT	X-ray Transmission

Literature

1. **Revised draft guidance on best available techniques and best environmental practices for the recycling and waste disposal of articles containing polybrominated diphenyl ethers listed under the Stockholm Convention;**

2. **Handbook of Plastics Recycling; Francesco Paolo La Mantia, Rapra Technology Limited (2002).**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