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TOWARDS A GENERIC PROCEDURE FOR THE DETECTION OF RELEVANT CONTAMINANTS FROM WASTE ELECTRIC AND ELECTRONIC EQUIPMENT (WEEE) IN PLASTIC FOOD-CONTACT MATERIALS: PRACTICAL ASPECTS

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FOOD CONTACT ARTICLES

are an important group of consumer goods mainly made of polymeric materials which are regulated within Europe by the EC. Regulation No. 10/2011 having in its annex 1 a whole list of constituents which are allowed to be used. Recently in black polymeric food contact items traces of brominated flame retardants (BFRs) have been detected indicating the presence of recycled polymers, mainly coming from waste electric and electronic equipment (WEEE) as BFRs are a main additive in electric and electronic applications. **This WEEE addition to food contact articles is illegal within the EU as traces of BFRs in polymer food contact articles are prohibited in the EU** (EC. Regulation No. 10/2011).

In a first study from 2013 bromine and BFRs have been confirmed to be presented in black food-contact articles in the EU. The reason for choosing black polymeric materials for this study came from our findings that the (grey) recycling melt can be fashionable upgraded by adding carbon black. As an argument that WEEE, as a mixture of several polymers, might be used in food contact materials is the detection of multiple BFRs (both: older ones and more recent alternatives). Another confirmation point is the trace amount of bromine which is too low to achieve flame retardancy.

MORE EVIDENCE ANNO 2014

In order to get more evidence that WEEE has been used for the production of polymeric food contact materials, several black polymeric kitchen utensils were purchased (n=10) on the European market and evaluated on more parameters:

- **XRF spectroscopy** (Shimadzu, EDX-800P) combined with **thermal desorption GC-MS** measurement (Frontier laboratories double shot pyrolyzer) allow to measure the overall bromine concentration and BFR presence.
- **ICP-OES** (Shimadzu, ICPE-9800, axial plasma): WEEE relevant Rare Earth Elemental content (REEs: Ce, Dy, Er, La, Nd, Pr and Y) and antimony levels (synergist flame retardant with bromine) after acid digestion.
- **FTIR spectroscopy** (Shimadzu, IRPrestige, ATR method) has been performed in order to detect foreign polymer content. In some cases the absorption signals were strong enough to detect e.g. polycarbonate in ABS.
- **Pyrolysis GC-MS** (same hardware as thermal desorption) was used to confirm the FTIR measurements as well as to detect specific fragments in order to prove the presence of other ``foreign`` polymers. The main matrixes were based on styrenic polymers (ABS) or polyolefins (PP/PE) as they have advantages in the recycling process.

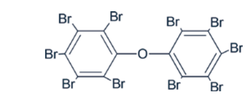
Overview of 10 selected black polymeric samples purchased in Europe (anno 2014) and results showing the macromolecular contaminants, bromine content, BFR identification, Sb content (synergist) and REE content.

Sample	Description	Main polymer (FTIR)	Detected monomers (Pyrolysis GC-MS)	Macromolecular contamination	Br content b (mg kg^{-1})	BFRs (Thermal desorption)	Sb content (mg kg^{-1})	Detected REEs
1	Egg cutter	PP/PE	4-ethenyl-cyclohexene; styrene; α-methylstyrene; Benzoic acid	HIPS/ PBT or PET	57	TBBPA, decaBDE	< 2	Ce, Dy, La, Nd, Pr, Y
2	Electric frying pan	PBT	1,4-butadiene; 4-ethenyl-cyclohexene; styrene; α-methylstyrene	HIPS or ABS or SAN	5975	TBBPA, DBDPE	504 ± 73	Ce,
3	Apple cutter	ABS	methylmethacrylate	PMMA	279	TBBPA, DBDPE, BTBPE	52 ± 2	-
4	Screwable part (thermocup cover)	PP/PE	Styrene; α-methylstyrene	PS/PBT or PET	66	TBBPA, decaBDE	< 2	Ce, Nd, Y
5	Movable lid (thermocup cover)	ABS	Methylmethacrylate; Benzoic acid	PMMA/ PBT or PET	504	TBBPA, decaBDE	114 ± 2	-
6	Movable lid (thermocup cover)	ABS	methylmethacrylate	PMMA PC, PP	1521	TBBPA, decaBDE, DBDPE	271 ± 40	-
7	Screwable part (thermocup cover)	PP/PE	Benzoic acid; 4-ethenyl-cyclohexene styrene; α-methylstyrene;	PBT or PET HIPS or ABS or SAN	< 40	-	< 2	-
8	Screwable part (thermocup cover)	PP/PE	Benzoic acid; styrene; α-methylstyrene	PBT or PET PS	< 40	-	< 2	-
9	Screwable closure (thermocup cover)	PP/PE	Benzoic acid; 4-ethenyl-cyclohexene; styrene; α-methylstyrene	PBT or PET HIPS or ABS or SAN	62	TBBPA, decaBDE	< 2	Dy, Nd
10	Screwable closure (thermocup cover)	PP/PE	Methylmethacrylate; styrene; α-methylstyrene	PMMA PS PBT or PET	< 40	-	< 2	-

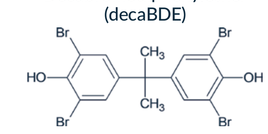
Further reading: Puype et al., Food Additives & Contaminants: Part A, 2015, 32 (3), p. 410-426

STUDY 2013

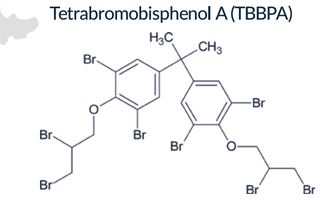
Detected BFRs:



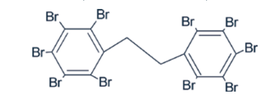
Decabromodiphenylether (decaBDE)



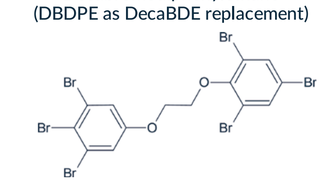
Tetrabromobisphenol A (TBBPA)



TBBPA-bis(dibromopropylether) (TBBPA-BDBPE)



Decabromodiphenylethane (DBDPE as DecaBDE replacement)

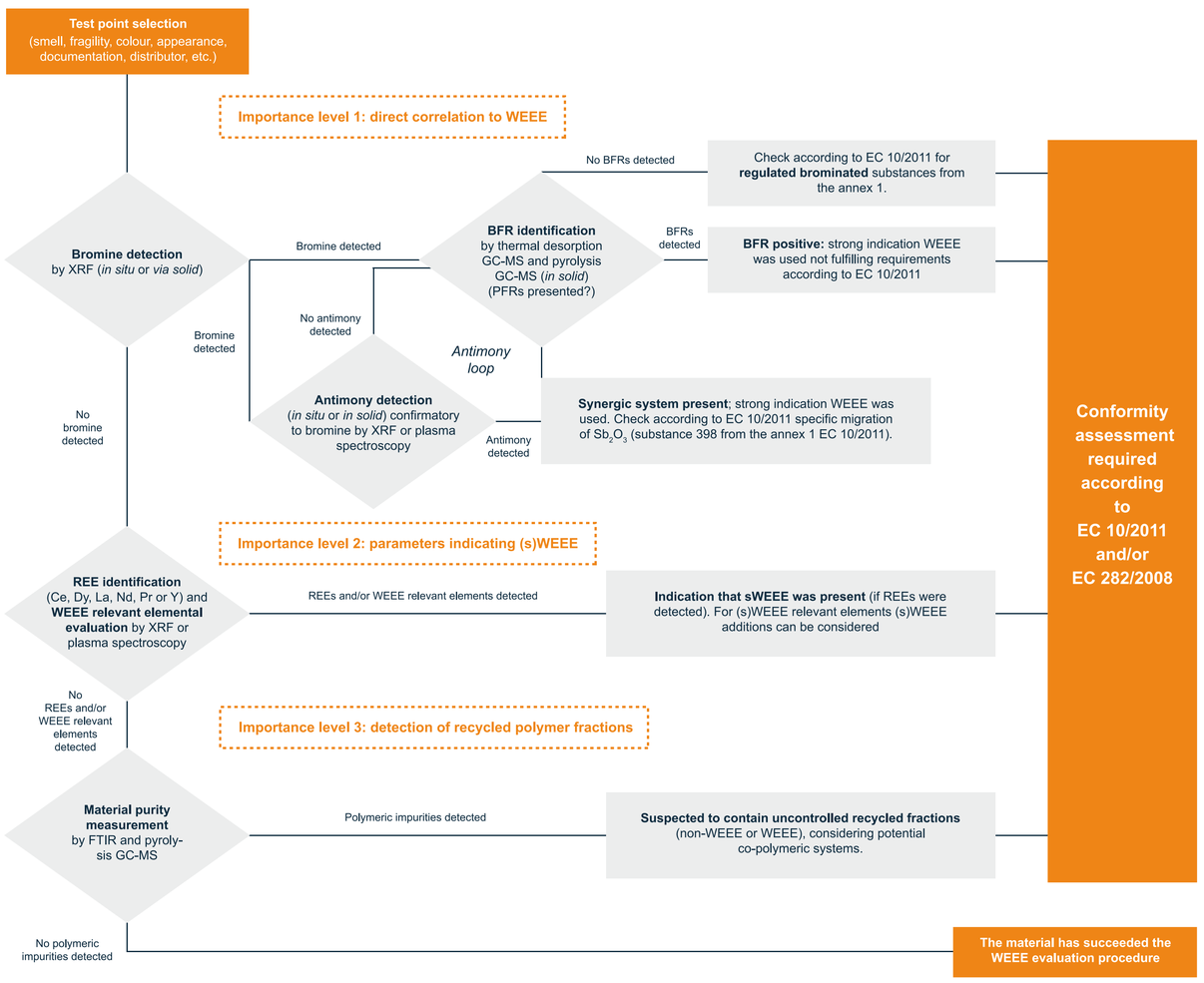


1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE)

Results from our pilot-study made in 2013 on the occurrence of brominated flame retardants in black thermo cups and selected kitchen utensils purchased on the European market by combining multiple analytical techniques: XRF spectroscopy (BFR presence); thermal desorption GC-MS (BFR identification) and FTIR analysis (polymer identification).

Samsonek and Puype, Food Additives & Contaminants: Part A, 2013, 30 (11), p 1976-1986

GENERIC PROCEDURE FOR THE DETECTION OF WEEE RELEVANT CONTAMINANTS



CONCLUSION

Our proposed generic procedure for the evaluation of WEEE in plastic FCMs, includes an antimony loop for the synergetic confirmation, and levels of importance, all taking into consider principles of Regulation (EU) 10/2011 (plastic FCMs) and (EC) 282/2008 (recycled plastic FCMs).

To the best of our knowledge, WEEE waste adding to plastic FCMs is illegal according to EC 10/2011, however, due to the lack on screening mechanisms there is still breakthrough of such articles on the market, therefore our generic procedure to quickly and effectively screen suspicious samples.

Further reading: F Puype et al. Food Addit Contam Part A Chem Anal Control Expo Risk Assess 34 (10), 1767-1783. 2017