Multi-Element Analysis of Relevant Elements and Macromolecular Contaminants in Black Polymeric Food-Contact Materials and it's Origin

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■ Overview

This poster focuses on several evidences that fractions of waste electrical and electronic equipment (WEEE) are presented in food-contact articles currently purchased on the European market. WEEE is an abbreviation covering the waste stream fraction containing all types of electrical goods. The determination of WEEE relevant substances in food-contact articles (FCAs) was achieved by applying several independent analytical methods where the researchers came to surprising results addressing the misuse of WEEE.[1]

Figure 1: Misuse of polymeric WEEE in food-contact articles

■ Samples – FCA's

Based on previous published work[2] (Samsonek et al., 2013) where the authors focused mainly on the detection of BFRs (brominated flame retardants) in food-contact articles (FCAs) like thermos-cups and several kitchen utensils purchased on the European market, in the actual study further material is investigated. By selecting the samples, special attention is given to black polymeric parts.

Black polymeric items have a high chance of being contaminated by recycled polymers like polymers from WEEE streams. Technically speaking, a melt of recycled polymeric material with virgin material does not look attractive, however, after colour unification with black pigments the black polymeric material look again attractive for the customer.

■ BFRs present?

BFRs are generally used in electronic equipment with the aim to inhibit, suppress, or delay the production of flames and as a consequence to prevent the spread of a fire.

At first all the samples screened by the fast and non-destructie XRF technique (Shimadzu EDX-800P), to check the presence of Br as a first indicator for BFR's or WEEE, resp.
7 of the 10 samples are classified as Br positive with amounts between 60 to 5980 mg/kg. The concentrations appear too low to sufficiently achieve flame retardancy and therefore it is assumed that a small fraction of Br containing polymers have been used during production.

By thermal desorption GC-MS (QP2010, Shimadzu) the Br positive samples were checked for presence of BFRs. In each Br positive sample decaBDE (decabromodiphenylether) and/or DBDPE (decabromodiphenylethane) was detected. Only in one case BTBPE was detected in combination with TBBPA and DBDPE.

So far, BFRs are not listed in the positive list of the European Food Safety Authority (EFSA) defining a specific migration limit for controlled migration and evaluation of the FCA and as a consequence, they are not allowed to be used as initial substances for the manufacturing of FCAs sold on the European market.

■ Element Analysis using ICPE-9820

The simultaneous ICPE-9820 (Shimadzu) with mini torch has been used, enabling axial and radial view for a high variety in detection of low and high concentrated elements. For axial view only, the ICPE-9810 is suitable.
The ICPE-9800 Series high-performance echelle optics is using a large scale CCD detector with 1024 x 1024 pixels and can determine all elements simultaneously within one single analysis.

The selected elements for monitoring were As, Be, Cd, Cd, Cu, Cr, Fe, Hg, Ni, Pb, Sb and Zn. For the analysis of REEs[3] Ce, Dy, Er, La, Nd, Pr and Y were selected due to their abundance in WEEE. The elements Hg and As are present at trace levels and thus have been measured using the hydride vapour technique.

Figure 2: New ICPE-9800 Series

For the evaluation if WEEE was used for the production of black FCAs Sb was presumed to be a key element. The results demonstrate that, in a majority of the cases, BFRs were present in combination with higher Sb concentrations. The concentration of Sb was in 4 of the 7 cases higher in FCAs containing BFRs which corresponds to the use of Sb_2O_3 as synergist flame retardant with halogenated FRs. In all cases when Br was detected at elevated concentrations (> 200 mg/kg of Br) Sb was detected as well.

In most of the BFR positive samples typical elements used in electronic equipment like ferrous elements and the selected heavy elements (As, Cd, Cr, Cu, Fe, Hg, Ni, Pb and Zn) were present either at trace level or at elevated concentrations (see excerpt in table 1).

Typical REEs (Ce, Dy, La, Nd, Pr and Y) found in many electronic and electric applications nowadays were present in 4 of the 7 Br positive samples while in Br negative samples no traces of REEs were detected.

■ Macromolecular Contaminants in FCAs

A destroying free screening of the polymers were done with ATR FTIR (IRPrestige-21, Shimadzu, equipped with reflectance diamond ATR unit). These spectra were compared with standard spectra from databases which are commercially available e.g. RoHS; ATRPolymer2; IRs Polymer2; T-Polymer2 all running on LabSolutions IR software (Shimadzu, Kyoto, Japan) combined with in-house libraries. In addition pyrolysis GC-MS has been used to identify the contaminants.

■ Results & Conclusion

As an example sample 2, which is a PBT (poly butylene terephthalate) drying pan sample, did contain Br at a level of 5980 mg/kg joined with a concentration of 504 mg kg-1 of Sb. The presence of Sb in PBT or PET can be justified as Sb_2O_3 is commonly used as a catalyst in such a matrixes, however, the presence of Sb and Br together is not common in PBT or PET applications unless to give flame retardancy. In this sample 2, it was expected that the addition of flame retarded HIPS/ABS or SAN fractions are causing the undesirable presence of these contaminants, all are styrenic co-polymers.

Table 1: ICPE-9820 Results of Sample 1, egg cutter. All data in [mg/kg]

As	Cd	Ce	Cr
3.98 ± 0.21	2.03 ± 0.03	8.94 ± 0.01	19.4 ± 0.5
Cu	**Dy**	**Fe**	**Hg**
37,30 ± 1,07	0.42 ± 0.01	58.8 ± 4.0	0.14 ± 0.01
La	**Nd**	**Ni**	**Pb**
2.40 ± 0.01	2.51 ± 0.01	2.99 ± 0.32	99.3 ± 0.9
Pr	**Y**	**Zn**	
4.54 ± 0.01	1.99 ± 0.01	101 ± 2	

The purpose of this study was to obtain analytical data by combining several analytical techniques in order to prove the undesirable use of WEEE hidden in black polymeric FCAs sold on the European market. Several indicators were discovered, underlining this statement. To read the whole paper, see reference 1 or scan the QR-code below.

■ References

[1] Puype F, Samsonek J, Knoop J, Egelkraut-Holtus M, Ortlieb M. 2015. Evidence of waste electrical and electronic equipment (WEEE) relevant substances in polymeric food-contact articles sold on the European market, Food Additives and Contaminants: Part A | DOI: 10.1080/19440049.2015.1009499
[2] Samsonek J, Puype F. 2013. Occurrence of brominated flame retardants in black thermo cups and selected kitchen utensils purchased on the European market. Food Additives and Contaminants: Part A: 30(11):1976-1986
[3] Knoop J, Opperman U, Schram J. 2014. Interference-Free Determination of REEs in Electronic Waste Using ICP Optical Emission Spectroscopy. J. Chem. Chem. Eng 8;635-640

In cooperation with:

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