Evaluation of Direct Analysis in Real Time – High Resolution Mass Spectrometry (DART-HRMS) for WEEE specific substance determination in polymers.

Puype F.[1], Ackermann L.[2]

[1]Institute for Testing and Certification, Zlin, Czech Republic, 76421, fpuype@itczlin.cz; [2]Center for Food Safety & Applied Nutrition, U.S. Food and Drug Administration (FDA), USA, MD 20740

Introduction

Recently, brominated flame retardants (BFRs) have been found in toys and food contact materials as a result of bad recycling practices where Waste Electrical and Electronic Equipment (WEEE) has been mixed with virgin polymeric non-WEEE material[1,2,3]. Antimony trioxide (Sb_2O_3) is used in plastics as a flame retardant synergist with halogenated compounds. Sb_2O_3 acts as a synergist by reacting with halogens (bromine) to form free-radical antimony halides slowing or halting radical propagation of flames[4]. Keeping this in mind, the bromine content/BFR identification joined with the antimony levels in the material can be seen as a confirmation for WEEE presence in a polymeric sample. Commonly, X-ray fluorescence (XRF) spectrometry of target elements (Br and Sb) can be used as a *proxy* for BFRs and Sb_2O_3 from WEEE, however, so far no analytical technique is used to detect both precursors at once on a very specific base, meaning targeting specific BFRs and Sb_2O_3 in one run[5]. Therefore, within the scope of this paper, Direct Analysis in Real Time - High Resolution Mass Spectrometry (DART-HRMS) has been chosen to potentially detect both WEEE precursors. This technique is very promising from several perspectives: it is faster than common extraction/analysis; it targets molecular species (organic and in certain cases volatile inorganics) and allows desorption-ionization directly off the surface on the sample directly. We would like to present our preliminary findings concerning the specificity, sensitivity of the method for WEEE detection. This all to answer the question: can DART-HRMS avoid mis-identification or false positives/negatives for WEEE contaminated polymeric materials at a relevant concentrations.

Materials and methods

Samples

Certain Electrical and Electronic Equipment (EEE), toys and food contact materials were selected which were already determined to be WEEE positive. This identification was based on their signals for Br and Sb by XRF spectroscopy (Oxford Instruments ED2000 Ag spectrometer, Oxfordshire, United Kingdom) using subtraction of the Kβ & Lβ lines from As/Hg as they interfere the bromine signal) and with known BFR composition as evaluated by thermal desorption GC-MS (Frontier TDU AS with Shimadzu QP2010P GC-MS, FASST Sim/Scan). Several samples were chosen to be identified by Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) as well. As a control measurement, the certified reference material ERM®-EC591 (JRC-IRMM, Geel, Belgium) which is a technical penta-bromodiphenylether (BDE), octa-BDE, deca-BDE and decabromobiphenyl (decaPBB) doped polypropylene in pellet form with an overall Br concentration of 2.08 ± 0.07 g kg^{-1} and an overall Sb content of 0.713 ± 0.022 g kg^{-1}.

DART-HRMS Method

DART is a novel ion source used in mass spectrometry performing at atmospheric pressure in the open laboratory environment. It does not need a specific sample preparation and can directly be used for the analysis of solid, liquid and gaseous samples in their native state. DART produces excited state species from the carrier gases which react with reagent molecules in the atmosphere (water, oxygen) to form ionization reagents, or occasionally, directly (Penning) ionize sample analytes (*e.g.* BFRs and other constituents). Gas phase or thermally desorbed molecules ionize readily as molecular or quasi-molecular species. With the aid of DART-HRMS, exact mass measurements can be done rapidly with higher resolution.

Within our study, the DART negative ionization process $M\text{-}H^-$, + O_2^-, radical anion`s and $-Br_2+O^-$ ion forms can be observed. We used the DART-SVP (IonSense Inc.) He configuration in the negative mode programmed at 250-500°C with a 0.6-1 cm DART-to-inlet gap, and ~0,2 c, DART-to-sample distance. For the detection we use the Q Exactive™ Hybrid Quadrupole-Orbitrap™ Mass Spectrometer (Thermo scientific; using: QE capillary 250-350°C, 140000 FWHM, automated gain control $1e^6$, 200 ms maximum inject time, , m/z 86-1300 range).

Firstly, non-WEEE contaminated blank polymer samples were measured, then individual BFR standards were introduced sequentially (including saturated aqueous and neat Sb_2O_3). Then separately, WEEE impacted polymers were analysed by DART-HRMS. Sampling was done using the dip-it capillary system for polymer scratches, confirmed with direct introductions of polymer pieces.

Results and discussion:

All BFR standards analysed by DART-HRMS yielded unique quasi-molecular ions, most sensitively in negative ion mode (*e.g.* TBBPA, Figure 1). As was expected not every BFR contained easily dissociated protons to yield deprotonated ions, but radicals and O_2 adducts allowed quasi molecular ions to be identified for each BFR standard's DART spectra.

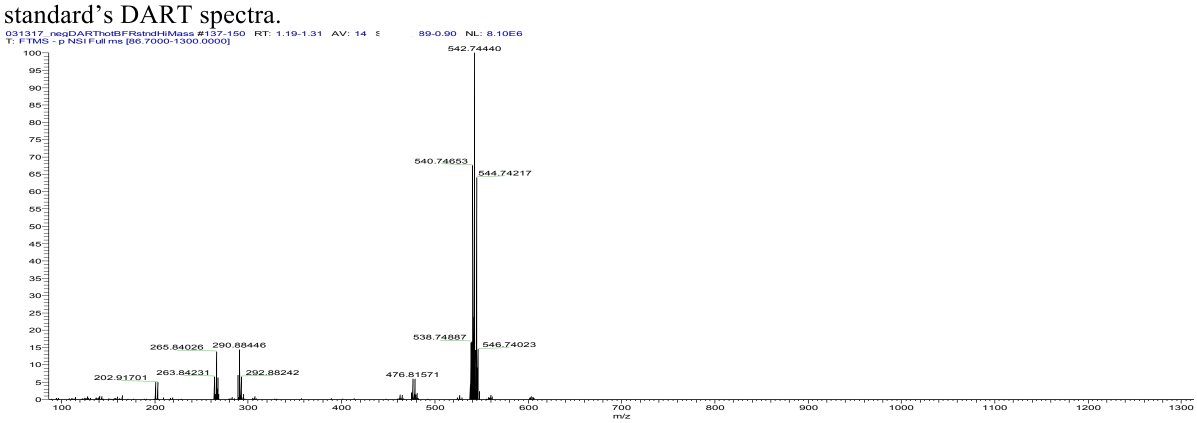

Figure 1: DART-HRMS spectrum (negative mode) of TBBPA ([TBBPA-H]-m/z 542.744).

Every BFR identified by thermal desorption GC-MS in the 9 WEEE containing polymers was readily identified in the same polymers by DART-HRMS. Initially, Initially, DART-HRMS looked promising to detect both BFRs and Sb_2O_3 as a proxy for WEEE detection. However, when looking for a Sb_2O_3 specific ion signal in the samples no peaks were detected. Partly the poor volatility of Sb_2O_3 could be the cause, however after several experiments, extra signals from more volatile halogenated Sb species were observed: m/z 242.813 $SbCl_3OH^{-\cdot}$ and m/z 260.779 $SbCl_4^{-\cdot}$ in pure Sb_2O_3 standards; m/z 378.658 $SbBr_3OH^-$ and m/z 440.573 from $SbBr_4^-$ in Sb_2O_3 containing polymers. Therefore we suggest that the Sb_2O_3 under the DART ionization conditions reacts in the gas phase with halogens (from flame retardants or elsewhere) and forms more stable antimony-halide anions which are readily detected in the negative mode. This is in strong concordance with the flame retardant literature and polymer-decomposition MS experiments.

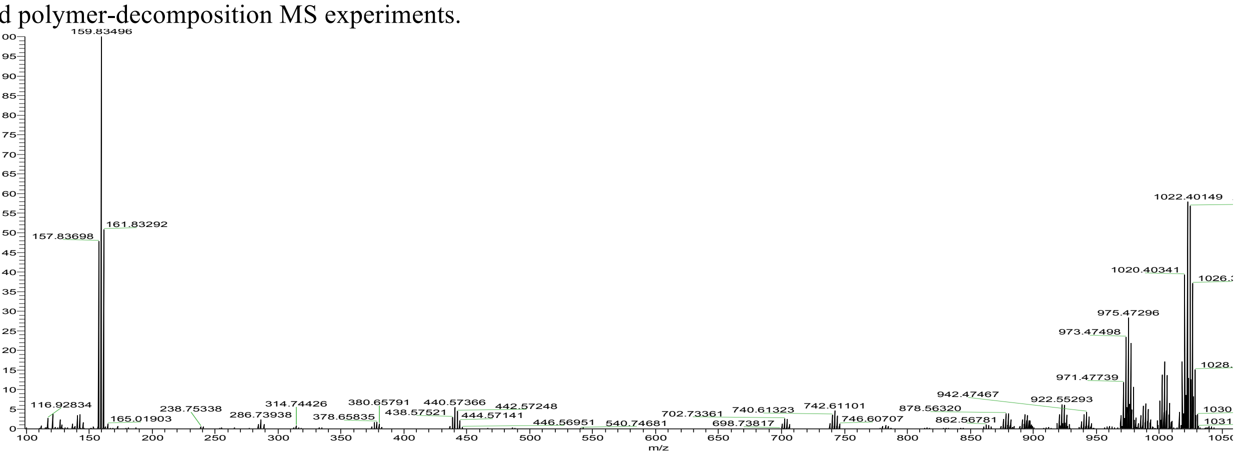

Figure 2: DART-HRMS spectrum (negative mode) of a green polyolefin pipe used for electronic cables containing TBBPA-DBPE (m/z 975 and 1022) and interaction products from the Sb_2O_3 additive with the BFRs were observed (m/z 378 SbBr3OH$^-$ and m/z 440 from SbBr4$^-$). The signals from Sb_2O_3 as a pure substance were not observed. The dibromide anion at M/e 159 has been observed as well.

The possible limitation is sensitivity, as not every Sb containing sample yielded antimony halide ions by DART-HRMS. This statement can be confirmed as the $SbBr_3OH^-$ and $SbBr_4^-$ signals have been detected in EEE samples (Figure 2 and 5, polyolefin pipes used for electronic cables) but were not always detected in the WEEE contaminated toy (Figure 3) and food contact samples (Figure 4). The certified reference material (ERM-591) containing BFR/Sb_2O_3 was carefully analysed by DART-HRMS (Figure 6) and beside the high Sb_2O_3 (0.713 ± 0.022 g kg^{-1}) content and the high Br (2.08 ± 0,07 g kg^{-1}) content the volatile antimony bromides ($SbBr_3OH^-$ and $SbBr_4^-$) were only once detected (1/6). Therefore DART-HRMS need some more optimization in terms of sample size, thermal desorption, or ion transfer efficiencies in order to routinely and reliably detect Sb in WEEE impacted polymer toys and food contact articles.

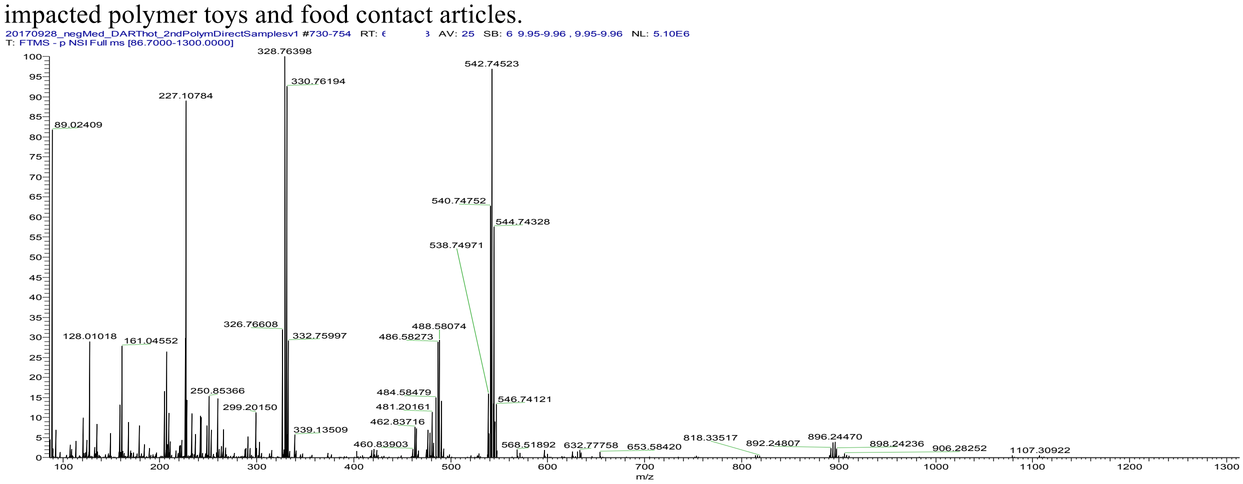

Figure 3: Direct DART-HRMS (negative mode) on a Toy (Rubik's cube) containing TBBPA (m/z 542), BTBPE (m/z 330), DBDPE (m/z 906) and decaBDE (m/z 488 and 896), however DART-HRMS could not reliably confirm the presence of Sb.

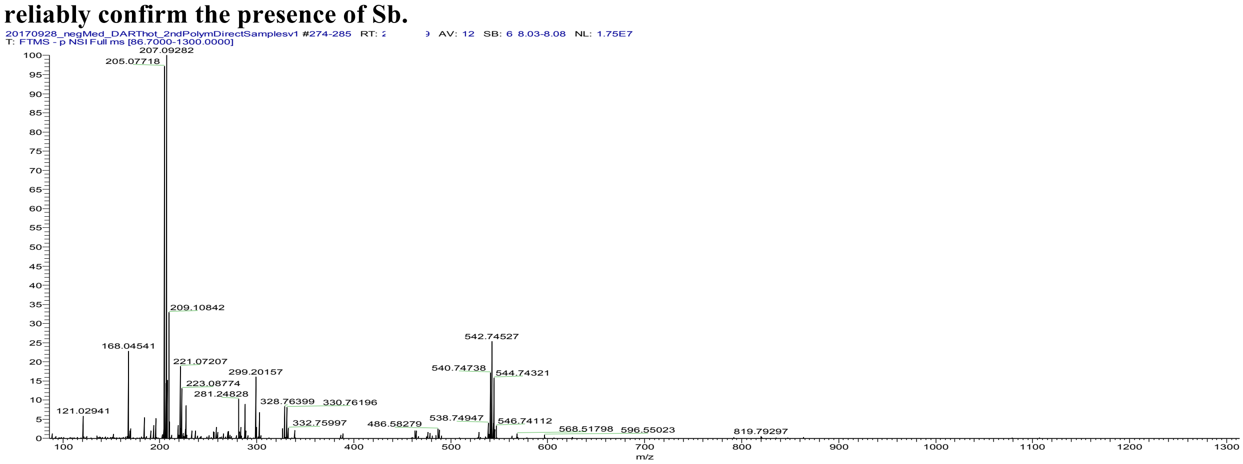

Figure 4: Direct DART-HRMS (negative mode) on a WEEE doped black ice bucket containing TBBPA (m/z 542), decaBDE (m/z 486 and 488) and BTBPE (m/z 328); (overall Br content 370 mg kg^{-1} and Sb 120 mg kg^{-1} measured by XRF), however DART-HRMS could not confirm the presence of Sb.

On the other hand, DART-HRMS was able to detect traces of multiple BFRs at once in all the evaluated samples (Figures 2, 3, 4 and 5). The detection of TBBPA, (1,2-Bis(2,4,6-tribromphenoxy)ethane) BTBPE and decaBDE together in one toy sample (Rubik's cube, Figure 3, acrylonitrile-butadiene-styrene polymer) increases the probability that several WEEE streams have been mixed, and provides evidence upon DART screening of WEEE contamination. As well in a food contact material (Ice bucket, Figure 4, acrylonitrile-butadiene-styrene polymer, 370 mg kg^{-1} Br and 120 mg kg^{-1} Sb) DART-HRMS could confirm TBBPA, decabromodiphenylethane (DBDPE) and decaBDE, where the overall bromine concentration has been measured at 370 mg kg^{-1} by XRF spectroscopy.

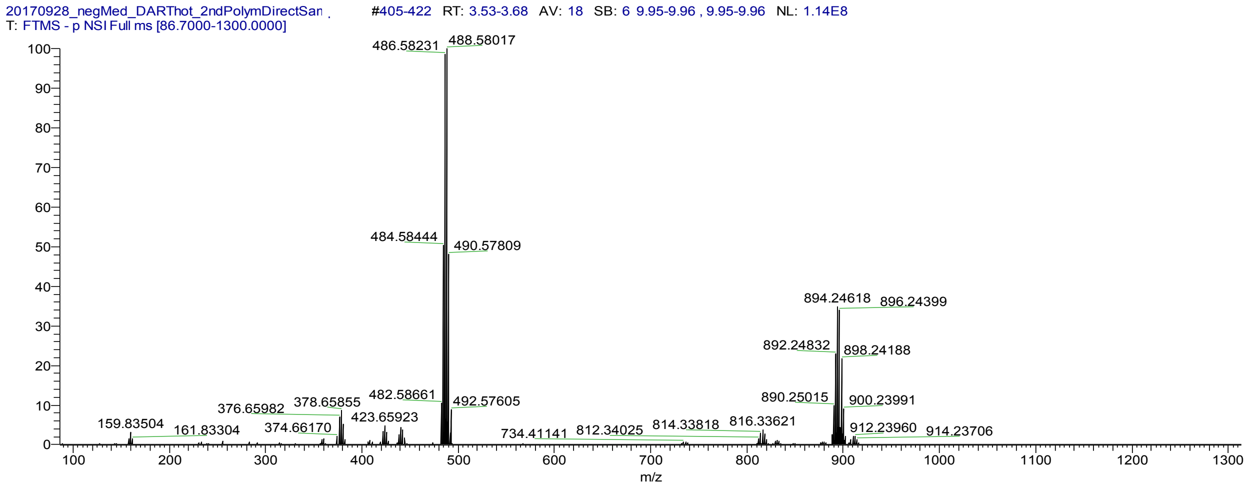

Figure 5: DART-HRMS spectrum (negative mode) of an orange polyolefin pipe used for electronic cables containing decaBDE (m/z 486 and 894) and interaction products from the Sb_2O_3 additive with the BFRs were observed (m/z 378 $SbBr3OH^-$ and m/z 440 from $SbBr4^-$). The signals from Sb_2O_3 as a pure substance were not observed.

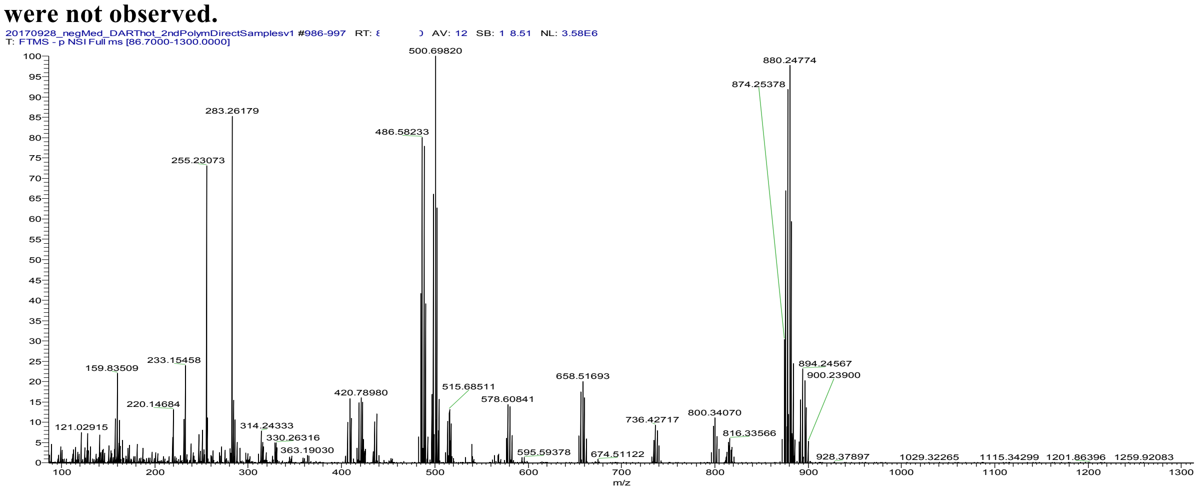

Figure 6: DART-HRMS spectrum (negative mode) of an EU-ERM-EC591 (polypropylene) containing decaBDE (m/z 486 and 894) and decaPBB (m/z 880 and m/z 500). The signals from Sb_2O_3 and Sb-Halides were not reliably observed.

DART-HRMS is able to screen for numerous BFRs as well as simultaneously the Sb based synergist at elevated concentrations. However, more efforts in the direction of sensitivity and synergist volatility (halogen interaction) have to be done to make this technique valuable for screening traces of WEEE in contaminated polymers from consumer goods like toys and food contact material. Concerning the identification BFR traces in polymeric toys and food contact articles DART-HRMS seems to be an applicable technique.

References:

1. Guzzonato A., Puype F., Harrad S.J. (2016), *Chemosphere*, 159:89-95
2. Martinho G., Pires A., Saraiva L., Ribeiro R. (2012) *Waste Management*, 32:1213-121
3. Puype, F., Samsonek, J., Knoop, J., Egelkraut-Holtus, M., Ortlieb, M. (2015) *Food Additives & Contaminants: Part A*, vol. 32: 410-426
4. Sato et al., (1998) *Polymer Degradation and Stability*, 62: 41-48
5. Puype, F., Samsonek, J. (2008) *Organohalogen Compounds*, vol.70: 1522–1525