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PUSHING THE LIMITS OF HAND-HELD X-RAY FLUORESCENCE SPECTROMETERS TO QUANTIFY BFRS IN WEEE

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Introduction

Processing of Waste Electrical and Electronic Equipment (WEEE) presents a potential risk to human and environmental health, in part due to the high brominated flame retardant (BFR) content of a substantial proportion of such items. BFRs such as polybrominated diphenyl ethers (PBDEs), polybrominated biphenyls (PBBs), hexabromocyclododecane (HBCDD) are restricted in WEEE at a level of 0.1 weight %. BFRs are a class of flame retardant additives (FRs) added to polymeric materials in a wide variety of consumer goods.1,2 PBDEs, PBBs, HBCDD, polybrominated diphenylethanes (PBDPEs), 1,2-bis(tribromophenoxy)ethane (TBPE), hexabromobenzene (HBB) and tetrabromobisphenol A (TBBPA) are common BFRs currently abundant in a large portion of the total stream of waste electrical and electronic equipment (WEEE) of the past thirty years 1. PBBs and PBDEs are applied as mixtures with compositions that broadly reflect the average degree of bromination, i.e. the three major technical mixtures of PBDEs commercially available are penta-BDE, octa-BDE and deca-BDE. 2 Due to the fact that BFRs are not covalently bound to the polymer chain they have the potential to easily migrate into the environment by volatilization or leaching.3 As a consequence, BFRs are ubiquitous in biota and human tissue samples due to their bioaccumulative and persistent behavior, with implications for human health.4-7

A guidance document published under the Stockholm Convention cites the need for best available technology (BAT) and best environmental practice (BEP) to be used in the recycling and disposal of articles containing POP-PBDEs, in order to reduce the risk of managing BFR-containing polymers and control the detrimental effects of such POPs on the environment by correctly separating them from the polymers that do not contain BFRs. The RoHS recast Directive 2011/65/EU that became effective in 2013 includes limit values for PBBs and PBDEs (classes covering the most largely used additive BFRs) at a maximum level of 0.1 weight % in homogeneous material. This recast is more focused than its predecessor directive on waste related criteria because poor waste management is being acknowledged as the root cause of contamination in new items. HBCDD is limited as a Substance of Very High Concern (SVHC) to the same levels in consumer goods via Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) legislation. The RoHS directive forces manufacturers to control the presence of RoHS relevant substances in their EEE components from the upstream perspective i.e. at the design and the procurement stage. The range of products falling under this directive is quite broad, comprising inter alia large and small household appliances, information technology and telecommunications equipment, consumer equipment, lighting equipment, electrical and electronic tools, toys, leisure and sports equipment, medical devices, and other EEE not covered by any of the categories given before.

Currently all the major BFRs intentionally added in the past to a wide range of consumer goods that required flame retardancy are now banned or restricted. Despite this, the same contaminants are now being found in an even wider range of goods that do not require flame retardancy, via their unintentional incorporation (via recycling) into items like kitchen utensils and food packaging,8 videotapes, children's toys and household products,9. To minimize such inadverted contamination, BFR-treated plastics should be separated during wasted treatment from the plastics that do not contain BFRs. Due to the costs and difficulties involved in their safe disposal, waste plastics thought to contain B are stockpiled, re-used in plastics that do not require a particular mechanical strength or incinerated10,11. These procedures lead mainly to two undesirable scenarios: (a) waste plastic that contains high percentages of BFRs is recycled by mixing with new ("virgin") polymers, thus increasing the quantity of new items contaminated with BFRs and making the future sorting process more laborious; and (b) when subjected to thermal treatment such as incineration, PBDEs may produce very toxic halogenated dibenzo-p-dioxins and dibenzofurans.12 RoHS compliance testing of WEEE requires measurements which should be performed in accordance with harmonized European standards in the EN 62321 series by the International Electrotechnical Commission (IEC). These standards give guidance on WEEE sampling, sample preparation methods and specific measurement methods. Generally, these standards describe

2 approaches: orientative screening and high-precision chemical analysis. The international standard related to RoHS testing for the BFR content in styrenic polymers requires GC-MS analysis (combined with laborious sample preparation procedures i.e. sub-sample grinding, cryo-grinding, solvent extraction, extract filtration, selective precipitation for oligomer removal, and chromatographic purification). However in many cases such analyses are hindered by the broad diversity of sample matrices resulting in unsatisfactory extraction efficiencies. Alternatively, as described in the test methods IEC 62321, if the individual characterisation of brominated compounds is not required, the overall bromine content can be screened using XRF as an "analytical procedure to determine the presence or absence of substances or compounds in the representative part of a product" 13.

Many developing countries receive substantial quantities of WEEE, but lack of resources and knowhow about the treatment procedures makes it very difficult achieve and monitor compliance with the relevant legislation and standards.. Thus, on one hand, the chemical analyses prescribed to produce BFR-compliant recycled plastics are difficult and prohibitively expensive, on the other hand the plastics must be somehow recycled or disposed to keep the activity economically viable and to meet legislative requirements - in Europe, Directive 2002/95/EC stipulates that at least 50% of collected WEEE must be recovered, reused or recycled. Rapid Br screening by XRF to provide pass/fail evaluation of legislative compliance is therefore an attractive option.14

In recent years, Energy Dispersive X-Ray Fluorescence (ED-XRF) technology incorporated into handheld instruments has offered substantial advantages in terms of detector sensitivity and resolution. Therefore this technique has become widely used to screen restricted substances. Hand-held XRF is a fast, non-destructive in-situ applicable technique that can give accurate and repeatable analytical results at a relatively low cost with a minimal use of consumables.15

As the concentrations of Br in BFR-containing WEEE are high (percentage levels), the low sensitivity of these instruments (ppm levels), does not constitute a problem for this application. XRF is considered reliable only for pre-screening or screening (IEC 62321) because of its technical limitations16,17 Moreover, XRF is only able to quantify the total elemental Br. Any analytical procedure that uses XRF for BFR quantification will always work on the assumption that all the detected Br is coming from organic compounds. Moreover, even if this assumption is correct, XRF is still susceptible to source misclassification– i.e. the incorrect assumption that all Br content is due to a specific (usually regulated) BFR, e.g. HBCDD, when some or all of the detected Br arises from the presence of another BFR. Of the alternative techniques, laser ablation, although promising, still requires optimisation for elemental analysis of polymers as this is a strongly matrix-dependent technique18.

This paper aims to develop an innovative, robust and reliable procedure using hand-held XRF for bromine quantification in polymers as an alternative BFR metric. To do so an ad-hoc calibration was developed with XRF and applied to the measurement of real samples. The resulting values were then cross-validated with LA-ICP-MS and also calibrated with bespoke standards, to ensure that the calibration matches with the matrix. Finally, to check the accuracy of hand-held XRF as a surrogate BFR metric, TD-GC-MS was performed on the samples to evaluate the qualitative distribution of different BFRs in each sample. In keeping with the focus of this study on easy, fast techniques, TD was used because solid samples like polymers can be directly measured by thermal desorption GC-MS and the sample preparation is practically solvent-free. Thermal desorption GC-MS has been proven to be an effective tool for identification of polymer additives (e.g. antioxidants, UV-stabilizers, initiators, plasticizers, etc.) as well as for the detection of BFRs.19

Making this method practically applicable was the priority of this study, therefore the calibration covers a wide dynamic range for Br concentrations, as the plastic casings for electrical and electronic equipment might contain BFRs from 0 to 30 weight %.20

Analytical Equipment

Hand-held XRF

A Thermo Scientific Niton XL3T Goldd Plus handheld device was used, equipped with a geometrically optimised large drift silicon detector and a 50 keV x-ray tube. The analysis was performed with a molybdenum filter, the emission fluorescence line chosen for quantification of Br was $K_{\alpha}1$ (11.92 keV) and the relatively less intense $K_{\beta}1$ was used for qualitative evaluation of the spectra (13.29 keV).

LA-ICP-MS

LA-ICP-MS was conducted using a Teledyne CETAC Technologies Analyte[™] G2 nanosecond excimer laser (ArF) hyphenated to a Thermo Scientific iCAP-Q ICP-MS. This short-WL laser has considerable advantages in increasing the amount of on-surface absorbed light over in depth-transmitted light 25,26 A

digital microscope (Keyence, Digitales Mikroskop VHS-600DSO) and a depth profiling tool (Mitutoyo SJ-410) were used for crater evaluation.

Thermal desorption GC-MS

For the identification of BFRs, a thermal desorption unit (Multi-Shot Pyrolyser EGA/PY-3030D, Frontier Laboratories LTD., Koriyama, Japan) equipped with a 48-position auto-sampler (Auto-Shot Sampler AS-1020E, Frontier Laboratories LTD., Koriyama, Japan) was interfaced with a GC-MS (GC-MS QP2010 Plus, Shimadzu, Kyoto, Japan). Several BFRs like higher brominated PBDEs are heat sensitive and may debrominate at elevated temperatures; therefore a short residence time is favoured on the separation column (Ultra ALLOY-PBDE; 0.25 mm inner diameter x 15 m; 0.05 μ m film of dimethyl polysiloxane, Frontier Laboratories LTD., Koriyama, Japan).

All samples were analysed in duplicate with further QA/QC provided by conducting multiple blank measurements to check for analyte carryover between samples. Method accuracy was assessed by analysis of a certified reference material (ERM-EC591, a polypropylene (PP) sample containing deca-BB, penta-, octa- and deca-BDE at realistic concentration levels (200-700 mg kg-1)). From the analytical point of view this method is limited to BFR identification and is not recommended for BFR quantification as polymers have a very diverse hardness. The variation in polymeric sample matrices results in variable extraction efficiencies for each BFR, making calibration for quantitative measurement of BFRs in different polymer matrices nearly impossible. Moreover, in recycled polymer fractions, debrominated, oxidised and hydrolysed substances appear and in some cases degradation products indicate the presence of originally added BFRs e.g. tribromobisphenol A indicates the presence of TBBPA. Hence, this method works mainly as a screening method for common BFRs and their degradation products. Target analytes are: PBBs, PBDEs, PBDPEs, HBCDD, TBBPA, tetrabromobisphenol A bis(2,3-dibromopropyl ether) (TBBPA-DBPE), bromophenols, BTBPE, tetrabromobisphenol A bismethylether (TBBPA-BME), HBB and other substances which can be identified in full scan mode (up to 1090 m/z) by electron impact ionization (70 eV) as this method uses the combination of full scan and single ion monitoring in one run. The method is capable of identifying BFRs down to a bromine level of 10 mg kg-1.

The Thermo Scientific Qtegra ISDS software platform was used for LA-ICP-MS data acquisition and evaluation. The Chromium software platform was used to control the Analyte G2 LA. For handheld XRF, the Thermo Scientific NDT software was employed to develop a calibration and empirical optimisation for Br.

For LA-ICP-MS the limit of detection was defined as 3 times the standard deviation of signal obtained for the blank (a bromine free ABS reference material). Background correction was achieved by selecting a 5 second region of interest (0-5 s) from the transient signal (laser off) and subtracting its mean intensity ('gas background') from the mean intensity of 79Br in the selected 12 seconds (laser on) region of interest (16-28 s): mean count rates are used instead of time integrated signals as the background and the region of interest for 79Br have different acquisition times.27 The uncertainty of each measurement (Relative Standard Deviation) was calculated as the SD between each sweep over the selected region of sample ablation required approximately 520 sweeps. Ten points per spectral peak were acquired and the most intense of those was selected for quantification. Measurement precision was calculated as the SD between two replicate line scans on different positions on the sample (but within the 8 mm diameter sampling area similar like XRF). For both these values the heterogeneity of the samples might give a contribution 28 the extent of which will vary with the elements analysed 29 Although cryogenic milling of the polymeric samples proved to reduce this influence on the RSD 29, it was not used in this study as it would defeat the purpose of an inexpensive technique with no sample preparation.

Equations correlating thickness and concentration with signal for XRF were derived in MS Excel and applied to the NDT software. Spectral precision was automatically calculated as two times the SD between each recursive measurement cycle performed during the sampling time. Analytical precision was calculated as the RSD between 4 repeated measurements. The 5:1 ratio between the two most intense spectral lines used for Br (K#1 and K#1) was used to correct for spectral interferences given by overlapping emissions (mainly from Zn and Al). The double counting effect (two photons with the same energy reaching the detector simultaneously and producing a response on the spectral line corresponding to double their energy) is corrected for by the firmware doubling the intensity of the line corresponding to exactly twice the K#1 for Br.

For XRF the LOD was calculated as three times the SD of ten replicate blank measurements (bromine free ABS reference material), with the LOQ calculated as 10 times that SD.

Results

An optimised method for Br quantification as a metric of brominated flame retardant (BFR) concentrations present in Waist of Electric and Electronic Equipment (WEEE) polymers is proposed as an alternative to the sophisticated, yet time consuming GC-MS methods currently preferred. A handheld X-ray fluorescence (XRF) spectrometer was validated with Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Customized standard materials of specific BFRs in a styrenic polymer were used in this study to perform an external calibration for hand-held XRF ranging from 0.08 to 12 weight % of Br cross-checking with LA-ICP-MS having similar LODs (0.0004 weight % for LA-ICP-MS and 0.0011 weight % for XRF). The "thickness calibration" developed in this study for handheld XRF and the resulting correction was applied on 28 real samples and showed excellent (R2=0.9926) accordance with measurements obtained via LA-ICP-MS, confirming the validity of hand-held XRF as an accurate technique for the determination of Br in WEEE plastics. This is the first study reporting the use of solid standards for the development of a thickness-corrected quantitative XRF measurement of Br in polymers using LA-ICP-MS for method evaluation. Thermal desorption gas chromatography mass spectrometry (TD-GC-MS) was used to confirm the presence of specific BFRs in the WEEE polymer samples studied. We propose that expressing limit values for BFRs in waste materials in terms of Br rather than BFR concentration (based on a conservative assumption about the BFR present), presents a practical solution to the need for an accurate, yet rapid and inexpensive technique capable of monitoring compliance with limit values in situ.