Improving the accuracy of hand-held X-ray fluorescence spectrometers as a tool for monitoring brominated flame retardants in waste polymers

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1 # Improving the accuracy of hand-held X-ray fluorescence spectrometers as a tool for

2 # monitoring brominated flame retardants in waste polymers

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4 An optimised method for Br quantification as a metric of brominated flame retardant (BFR) concentrations present in Waste of Electric and Electronic

5 Equipment (WEEE) polymers is proposed as an alternative to the sophisticated, yet time consuming GC-MS methods currently preferred. A hand-held X-ray

6 fluorescence (XRF) spectrometer was validated with Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS). Customized standard

7 materials of specific BFRs in a styrenic polymer were used to perform an external calibration for hand-held XRF ranging from 0.08 to 12 weight% of Br, and

8 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 here

9 for hand-held XRF and the resulting correction was applied to 28 real samples and showed excellent (R^2=0.9926) correlation with measurements obtained

10 via LA-ICP-MS. This, confirms the validity of hand-held XRF as an accurate technique for the determination of Br in WEEE plastics. This is the first use of solid

11 standards to develop a thickness-corrected quantitative XRF measurement of Br in polymers using LA-ICP-MS for method evaluation. Thermal desorption gas

12 chromatography mass spectrometry (TD-GC-MS) was used to confirm the presence of specific BFRs in WEEE polymer samples. We propose that expressing

13 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

14 practical solution to the need for an accurate, yet rapid and inexpensive technique capable of monitoring compliance with limit values *in situ*.

15 ## 1. Introduction

16 Processing of waste electrical and electronic equipment (WEEE) presents a potential risk to human and environmental health, in

17 part due to the high BFR content of a substantial proportion of such items. BFRs such as polybrominated diphenyl ethers

18 (PBDEs), polybrominated biphenyls (PBBs), and hexabromocyclododecane (HBCDD) are restricted in WEEE at a level of 0.1

19 weight%. BFRs are a class of flame retardant additives (FRs) added to polymeric materials in a wide variety of consumer goods

20 (Petreas et al., 2009; La Guardia et al. 2006). PBDEs, PBBs, HBCDD, 1,2-*bis*(tribromophenoxy)ethane (TBPE), hexabromobenzene

21 (HBB) and tetrabromobisphenol A (TBBPA) are common BFRs currently abundant in a large portion of the total stream of WEEE

22 generated over the past thirty years (Petreas et al., 2009). PBBs and PBDEs are applied as mixtures with compositions that

23 broadly reflect the average degree of bromination, *i.e.* the three major technical mixtures of PBDEs commercially available are

24 Penta-BDE, Octa-BDE and Deca-BDE (La Guardia et al. 2006). As in many applications, BFRs are not covalently bound to the

25 polymer chain, they have the potential to easily migrate into the environment by volatilization or leaching and because of their

26 bioaccumulative and persistent behaviour, most of them are classified as Persistent Organic Pollutants (POPs) (Hale et al., 2006;

27 de Wit et al.,2010; Covaci et al., 2006).

28 The RoHS recast Directive 2011/65/EU limits values for PBBs and PBDEs at a maximum of 0.1 weight% in homogeneous material

29 and focusses on waste related criteria acknowledging poor waste management as the root cause of contamination in new items.

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. Despite this, such chemicals are now being found as unintentional contaminants in a wide range of goods that do not require flame retardancy, via accidental incorporation (via recycling) into items like kitchen utensils and food packaging, (Samsonek et al., 2013) videotapes, children's toys and household products (Ashton et al., 2009). To minimise such inadvertent contamination, BFR-treated plastics should be separated during waste sorting and dismantling from BFR-free plastics, as prescribed in Stockholm Convention's best available technology (BAT) and best environmental practice (BEP) . Currently, many waste plastics thought to contain Br are stockpiled, re-used in plastics that do not require a particular mechanical strength, or incinerated (Schlummer et al., 2006). These procedures result in two undesirable scenarios: (a) waste plastic containing high percentages of BFRs is recycled by mixing with new ("virgin") polymers, thus increasing the quantity of new items contaminated with BFRs and impeding their elimination from the waste stream; and (b) thermal degradation of PBDEs into highly toxic halogenated dibenzo-*p*-dioxins and dibenzofurans (Sakai et al., 2001). European Standards (IEC62321-3-1) give guidance on WEEE sampling, sample preparation methods and specific measurement methods. Generally, they describe 2 approaches: total elemental screening and compound specific quantification; the latter typically 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). Alternatively, as described in the test methods IEC 62321, if characterisation of individual brominated compounds is not required, the total elemental bromine content can be measured using Energy Dispersive X-Ray Fluorescence (ED-XRF) technology incorporated into hand-held instruments as an "analytical procedure to determine the presence or absence of substances or compounds in the representative part of a product" (IEC62321-3-1).

The European Directive 2002/95/EC stipulates that at least 50% of collected WEEE must be recovered, reused or recycled (according to the concentration and nature of present contaminants), although the complexity and cost of traditional compound-specific analysis are not justified by the value of the analyzed items. Rapid Br screening by XRF to provide pass/fail evaluation of legislative compliance is therefore an attractive option (EC No 1907/2006).

Hand-held XRF is a fast, non-destructive *in-situ* applicable technique that can give accurate and repeatable data at relatively low cost and minimal use of consumables (Kalnicky et al., 2001).

As concentrations of Br in BFR-containing WEEE are high (percentage levels), the low sensitivity of these instruments (ppm levels), is not problematic for this application. However, XRF is considered reliable only for pre-screening or screening (IEC 62321) because of its technical limitations, summarised in Table 1 (Stockholm Convention, 2015; MacLeod et al., 2010). Moreover, XRF is only able to quantify total elemental Br. Any analytical procedure that uses XRF for BFR quantification will always work on the assumption that all the detected Br originates from organic compounds:a reasonable assumption considering Br salts are rarely found in polymers. Furthermore XRF is still susceptible to source misclassification– i.e. the incorrect

61 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

62 from the presence of another BFR. Of the alternative techniques, laser ablation, although promising, still requires optimisation

63 for elemental analysis of polymers as this -as XRF- is strongly matrix-dependent (Košler, 2008).

64 This paper reports an innovative, robust and reliable procedure using hand-held XRF for bromine quantification in polymers as

65 an alternative BFR metric. To ensure accuracy and minimise issues in XRF analysis, such as false negatives and negative errors

66 (Gallen et al., 2014), specially designed solid reference materials are used, the geometry and chemical composition of which are

67 key to a good matrix-matched calibration and error correction that enables XRF to quantify rather than simply screen bromine in

68 polymers. The resulting values were then cross-validated with LA-ICP-MS - also calibrated with bespoke standards- to ensure that

69 the calibration matches with matrix.. Finally, to roughly evaluate the qualitative distribution of different BFRs amongst samples,

70 TD-GC-MS was performed. In keeping with the focus of this study on easy, fast techniques, although TD does not provide

71 compound specific quantitative results it was used because solid polymers can be directly measured by TD-GC-MS resulting in

72 practically solvent-free sample preparation. TD-GC-MS is a proven effective tool for detection of BFRs in polymers, being able to

73 highlight bad recycling practices by evaluating the presence of different BFRs typically not used in combination, or not required

74 in a class of consumer' products (Bart, 2001).

75 Making this method practically applicable was the priority of this study, therefore the calibration covers a wide dynamic range

76 for bromine concentrations, as the plastic casings for electrical and electronic equipment might contain BFRs from 0 to 30

77 weight% (POP Review Committee, 2010).

78 **2. Materials and methods**

79 *2.1 Reference materials*

80

81 The first step of this study was to design and verify ABS reference materials (RMs) that fulfil the requirements of XRF and LA-ICP-

82 MS analysis containing realistic elemental compositions. The literature shows how, even with optimal ablation conditions,

83 quantification can be difficult due to the lack of appropriate calibration standards (Stehrer et al., 2010). To account for the strict

84 matrix dependence of these two techniques (see SI, 1. Matrix dependence) the RMs must:

85 - be made of the same plastic as samples;

86 - cover a wide calibration range from very low to very high concentrations of BFRs, to account for plastic that contains both

87 unintentionally (e.g. those present in plastic that while not directly flame retarded, contains recycled material that was) and

88 intentionally added BFRs;

89 - be homogeneous: in order to exclude intensity fluctuations due to local concentration changes during the laser ablation (Mans

90 et al., 2009);

91   -   contain also BFR co-synergist and other elements commonly used as additives in the plastics under test (e.g. Sb_2O_3 , $CaCO_3$,

92   TiO_2) (Jakab et al., 2003; Encyclopedia of polymer Science and Technology, 2013).

93   - have a similar sample mass absorption coefficient for X-rays and be representative of the different ablation behaviour due to

94   the presence of inorganic fillers in polymers as described by Todoli' et al.; and

95   - have a flat surface: XRF works under the assumption of Sherman's geometry, when the surface of the sample is not flat these

96   assumptions may fail (Mans et al., 2007).

97   The standards were produced according to these specifications by Fachhochshule Muenster Labor für Instrumentelle Analytik

98   (FMLIA). The method used to produce and test the standards is described in detail elsewhere (Mans et al., 2009) but a brief

99   summary is provided in the SI (2. Solid reference material: preparation and testing). Deca-BDE was added in 9 different

100   concentrations producing 9 RMs, individually melted into solid cylindrical discs with a diameter of 40 mm at 5 different

101   thicknesses.

102   *2.2 Sampling*

103   28 samples of various items of EEE were collected from different locations (SI, Table 2), with a preference for styrenic polymers

104   such as acrylonitrile butadiene styrene (ABS) and high impact polystyrene (HIPS) as they cover the vast majority of the polymers

105   used for these appliances (Stockholm Convention, 2015).

106

107   2.3 Sample preparation and extraction

108

109   For hand-held XRF, samples were wiped with ethanol, their thickness measured with a digital calliper and then cut into pieces of

110   at least 8 mm diameter. For LA-ICP-MS, samples analysed previously by hand-held XRF were grouped into two analytical batches

111   based on Br concentration: low (<LOD - 0.8 weight%) and high (1.6 – 12 weight%) concentration and placed into the ablation cell.

112   The samples were divided into two batches to minimise background generated by evaporation of low boiling BFRs.

113   For TD-GC-MS, samples were cut into smaller *ca.* 2 mm cubes and 0.2 g of sample was dissolved/leached in 1 mL toluene

114   (GC/ECD-grade residue analysis, Chromservis s.r.o., Prague, Czech Republic). For extraction of BFRs, toluene was chosen as it

115   enables high extraction yields for all targeted BFRs. Our TD method is described in detail elsewhere (Hosaka et al., 2005; Puype

116   et al. 2015; Puype et al., 2008), but a brief summary is provided (in the SI, 3. TD-GC-MS Method and Sample Preparation).

117

118   *2.4 Hand-held X-Ray Fluorescence Spectrometry*

119

120 A Thermo Scientific Niton XL3T Goldd Plus handheld device was used, equipped with a geometrically optimised large drift silicon

121 detector and a 50 keV x-ray tube. The analysis was performed with a molybdenum filter, the emission fluorescence line chosen

122 for quantification of Br was Kα1 (11.92 keV) with the relatively less intense Kβ1 used for qualitative evaluation of the spectra

123 (13.29 keV) (see SI, Table 3 for details). Proprietary Thermo Scientific NDT software was employed to develop a calibration and

124 empirical optimisation for Br.

125 Equations correlating thickness and concentration with XRF signal were derived and applied to the NDT software. Spectral

126 precision was calculated as two times SD between each recursive measurement cycle performed during the sampling period.

127 Analytical precision was calculated as the RSD of 4 repeated measurements. The 5:1 ratio between the two most intense spectral

128 lines used for Br (Kα1 and Kβ1) was used to correct for spectral interferences given by overlapping emissions (mainly from Zn

129 and Al). The double counting effect (two photons with the same energy reaching the detector simultaneously and producing a

130 response on the spectral line corresponding to double their energy) is corrected for by the firmware doubling the intensity of the

131 line corresponding to exactly twice the Kα1 for Br.

132 For XRF the LOD was defined as in ICH1 Guidance (Q2,R1: Validation of Analytical Procedures) as three times the SD of ten

133 replicate blank measurements (bromine free ABS reference material), and the LOQ calculated as 10 times that SD.

134

135 *2.5 Laser Ablation-Inductively Coupled Plasma-mass spectrometry*

136

137 LA-ICP-MS was conducted using a Teledyne CETAC Technologies Analyte™ G2 nanosecond excimer laser (ArF) hyphenated to a

138 Thermo Scientific iCAP-Q ICP-MS. This short-wavelength laser has considerable advantages in enriching the amount of on-surface

139 absorbed light relative to in-depth transmitted light (Guillong et al., 2003; Gonzales et al., 2002). A digital microscope (Keyence,

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

141 Thermo Scientific Qtegra ISDS software was used for LA-ICP-MS data acquisition and evaluation, while Chromium software was

142 used to control the Analyte G2 LA. Background correction was achieved by selecting a 5 second region of interest (0-5 s) from the

143 transient signal (laser off) and subtracting its mean intensity ('gas background') from the mean intensity of ^{79}Br in the selected 12

144 seconds (laser on) region of interest (16-28 s): mean count rates are used instead of time integrated signals as the background

145 and the region of interest for ^{79}Br have different acquisition times (Longerich et al., 1997). The uncertainty of each measurement

146 (expressed as relative standard deviation - RSD) was calculated as the SD between each sweep over the selected region of

147 interest divided by the mean count rate in that region and multiplied by 100. A 20 second measurement of sample ablation

148 required approximately 520 sweeps. Ten points per spectral peak were acquired with the most intense of those selected for

149 quantification. Measurement precision was calculated as the SD between two replicate line scans on different positions on the

150 sample (but within the 8 mm diameter sampling area similar to XRF). For both these values the heterogeneity of the samples

might give a contribution (Danyushevsky et al., 2011) which will vary with the element analysed (Stehrer et al., 2010). Although cryogenic milling of the samples has been proven to reduce this influence on the RSD (Stehrer et al., 2010), it was not used in this study as doing so would defeat the purpose of an inexpensive technique with no sample preparation. The LOD for this technique was calculated as three times the SD of the blank response (Br-free RM) divided by the slope of the calibration curve, according to ICH1 Guidance (Q2,R1: Validation of Analytical Procedures) A polyatomic plasma-based interference for ^{79}Br is given by $^{40}Ar^{38}Ar^1H^+$, $^{40}Ar^{39}K^+$, $^{31}P^{16}O^{3+}$ and for ^{81}Br by $^{40}Ar^{40}Ar^1H^+$, $^{32}S^{16}O^3H^+$ and $^{33}S^{16}O^{3+}$. To remove these interferences the collision reaction cell of the ICP-MS was pressurised with a mixture of 7 v/v% H_2/He as collision gas in order to perform kinetic energy discrimination on the unwanted polyatomic interferences. Br was quantified based upon ^{79}Br signal intensity with ^{81}Br measured to evaluate deviations from the ^{79}Br to ^{81}Br isotopic ratio. It can be assumed that oxides and polymer samples vaporise at different depths into the ICP, giving a different ionisation yield. As this study focuses on Br determination as a surrogate metric for BFRs, we chose to optimise the sampling depth especially for Br (present as an organic species), which was a trade-off against the quantification of other elements (e.g. Sb and Ti) present as oxides in the reference materials. For this reason and also because of poorer homogeneity of these oxides (see SI, 2. Solid Reference Material: preparation and testing), Sb and Ti were excluded from subsequent evaluations.

2.6 Thermal desorption Gas Chromatography-mass spectrometry

For the identification of BFRs, a TD 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 μm dimethyl polysiloxane film, 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 decabromobiphenyl, along with Penta-, Octa- and Deca-BDE at realistic concentration levels (200-700 mg kg^{-1})). This method is limited to BFR identification, and not recommended for BFR quantification as polymers possess 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 very difficult. 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, HBCDD,

182 TBBPA, tetrabromobisphenol A *bis*(2,3-dibromopropyl ether) (TBBPA-DBPE), bromophenols, BTBPE, tetrabromobisphenol A

183 *bis*methylether (TBBPA-BME), HBB, and other substances which can be identified in full scan mode (up to 1090 *m/z*) by electron

184 impact ionization (70 eV) as this method uses the combination of full scan and single ion monitoring in one run. The method is

185 capable of identifying BFRs down to a bromine level of 10 ppm.

186 ## 3. Results and discussion

187 *3.1 Development of ad-hoc thickness correction for ABS with XRF*

188 This calibration approach comprised measuring the intensities non-corrected for thickness for each concentration level of the

189 solid reference materials at different thicknesses. These concentration values were plotted against thickness (Fig. 1). The

190 obtained "thickness calibration curve" showed similarities with the exponential Attenuation Law for photons in matter (Lambert

191 Law of Absorption).Therefore, a generic negative exponential function (1) was chosen as the starting point for our model.

192
$$I = cI_0 \cdot \left(a - e^{-b \cdot D}\right) \tag{1}$$

193 Where I=signal; I_0=signal for infinite thickness; D=thickness in mm; a is a parameter regulating the offset with respect to the y

194 axis; b is a function of the material in terms of mass absorption: defined as the linear absorption coefficient. The inverse of b, is

195 what we defined as "infinite thickness", to which corresponds the concentration value found on the plateau of the exponential

196 function (N.B. the assumption that b remains constant when the Br concentration changes is an approximation); and c is the

197 parameter that regulates the slope of the unsaturated region of the function. To fit this equation to our empirical results, these

198 parameters were varied recursively until the squared deviation was minimised (using Excel's 'Solver' algorithm). The value of *b*

199 was found to be 0.26, hence the calculated "infinite thickness" (1/*b*) was 3.85 mm which, in fact, from the graph in Fig. 1 looks to

200 be the starting saturation point. Once the parameters for this equation were calculated, it was solved for I_0 in order to adjust the

201 uncorrected signal *I* to the sample thickness (2).

202

$$I_0 = \frac{I}{c \cdot (a - e^{-b \cdot D})} \tag{2}$$

203

204 Hence, for given values of signal intensity and thickness of the sample, the equation returns the value of intensity corresponding

205 to the "infinite thickness" (see Fig. 1).

206 The accuracy of this method was evaluated by comparing the corrected values obtained from the thickness calibration and the

207 reference values, according to the formula (3):

208

210

211 Average accuracy without thickness correction for thin layers (1-3 mm) was 82.8%, while after the thickness correction the

212 accuracy is improved to 93.9%. This value is satisfactory considering that a value of 89% on one single- controlled standard was

213 obtained in a very recent study (single measurement)(Igzi et al., 2015). We next evaluated the method uncertainty (precision) as

214 the SD between four replicates. For RMs this value is independent on the homogeneity of the material (because both macro and

215 micro homogeneity were tested for these RMs). Differences between measured RMs and their reference concentrations were

216 always within the measurement uncertainty (Fig. 2). The LOD was 0.0011%, while LOQ was 0.0036%.

217

218 *3.2 Method development and matrix matched calibration with LA-ICP-MS*

219 After tuning the ablation parameters and the ICP parameters (see SI, Table 4 and 5), calibration was performed with the nine

220 RMs containing different concentrations of Br (see SI, Table 1).

221 An initial attempt was made to place all the RMs and samples in the ablation cell. Unfortunately the background produced by the

222 higher Br concentration RMs and samples was too high to obtain valuable information out of the lower concentration samples

223 as described in the section 2.3 Sample preparation and extraction. Consequently, a calibration was first performed on the four

224 low concentration RMs (0%, 0.08%, 0.4% and 0.8% Br,See SI, Fig. 5). The equation fitting this plot was used to translate into

225 concentrations the count rates of ^{79}Br in the low concentration samples placed in the cell together with the low concentration

226 RMs. The same procedure was followed for the high concentration RMs (1.6%, 2.4%, 5.7%, 8.0% and 12.0% Br) placed in the cell

227 with high concentration samples (See SI, Fig.5). For the low Br concentration batch the R^2 was 0.9990, while for the high Br

228 concentration batch, R^2 was 0.9986.

229 The average accuracy obtained for the reference materials (calculated using equation (3)) was 93.3%, with lowest values of

230 78.8% and 79.2% obtained for the two RMs that have a concentration of Sb equal or exceeding that of Br. This suggests a

231 negative influence of Sb on measurements of Br. It has been shown (Evans et al., 1993) that the matrix effect depends on the

232 concentration of the matrix-element itself rather than the matrix-element to analyte-element ratio, so this loss of accuracy is

233 more likely ascribable to a particle effect. For each RM the difference between the measured value and the reference was within

234 the measurement uncertainty (SM, Fig. 6). The LOD for ^{79}Br was 0.0004% while LOQ was 0.0012%.

235 *3.3 Comparison between XRF and LA-ICP-MS Br data*

236 The Br data measured by XRF and LA-ICP-MS displays excellent accordance (Fig. 3, inset graph) and the XRF thickness correction

237 accounted for up to 46% increase in measured Br. The differences in Br concentrations between these techniques fall within

238 analytical uncertainty (RSD of each measurement for LA-ICP-MS, 2σ error for XRF; error bars in Fig. 3) for most samples. For LA-

239 ICP-MS the average precision for all samples given by the RSD between two line scan replicates was 5.9%; for XRF it was 1.5%.

240 The average RSD of [79]Br counts on each line scan was 10.7% (although better results have been observed in specific

241 measurements) a reasonably good value compared with: (a) an RSD of 15% obtained elsewhere for Br in line scans on polymers

242 (Izgi et al., 2005), (b) prior literature on line scans on polymers (Stehrer et al., 2010), and (c)raster scans of styrenic polymers

243 (Marshall et al., 1991). Moreover, a higher RSD based on the measurement points of a line scan with respect to the RSD

244 calculated between two line scan repetitions, corroborates the hypothesis of micro-homogeneity of the samples exerting a

245 greater influence on the time signal fluctuations. As expected, the LOD for LA-ICP-MS was almost a factor of 3 better than XRF

246 (LOD for LA-ICP-MS was 0.0004% and 0.0011% for XRF) and overall satisfactory for LA-ICP-MS considering the matrix and the

247 high ionisation potential of Br. In a recent study (Izgi et al., 2005) the LOD for LA-ICP-MS determination of [79]Br was as 0.0612% in

248 plastic. The accuracy of both techniques (XRF and LA-ICP-MS) is comparable (respectively 93.9% and 93.3%) while high

249 accordance between data produced by both techniques demonstrates our XRF thickness correction represents an improvement

250 on previous use of hand-held XRF for Br screening on polymers that reported false positives using XRF (e.g. Gallen et al., 2014).

251 Moreover, our method delivers quantitative determination of Br in WEEE using hand-held XRF.

252 *3.4 Results for TD-GC-MS*

253 The BFRs most frequently detected in our WEEE samples are Deca-BDE and TBBPA (SI, Table 6). Generally, samples contained

254 one or two different BFRs; however, in some cases several different BFRs were detected. This suggests the use of recycled WEEE

255 fractions in such samples, and highlights the potential for source misclassification whereby a Br signal may be incorrectly

256 attributed to a single specific regulated BFR. Our data also confirm the majority of old monitor casing samples to contain BFRs,

257 while more recent appliances show a higher number of Br-free polymers

258 4. Conclusions

259 Empirical corrections and tuning for hand-held XRF and LA-ICP-MS provided more accurate and precise Br data for WEEE plastics

260 compared with uncorrected data and recent literature on Br analysis in polymers using LA-ICP-MS and XRF (Izgi et al., 2015).

261 Therefore, automating these analytical techniques would greatly benefit Br analysis. Key findings from our study are that Br

262 quantification by hand-held XRF can be improved substantially by use of a matrix matched thickness correction; the matrix matched

263 calibrations presented here yielded excellent correlation between Br data obtained for the same samples using hand-held XRF

264 and LA-ICP-MS. This suggests hand-held XRF constitutes an accurate, rapid, inexpensive technique for on-site quantification of Br

265 in WEEE plastics; finally, TD-GC-MS detected in many samples only one or two BFRs, however in some cases a mixture of 3 or 4

266 BFRs was found. The presence of several BFRs in one sample may indicate the presence of a WEEE recycled fraction.

267   This simplified BFR quantification cannot remedy illegal dumping in landfills (where single-item screening would not be

268   practically possible), but it is an easy to operate, accurate, affordable, rapid method that may provide an appropriate solution in

269   recycling and sorting plants as well as control laboratories. In particular, XRF screening has potential for use in dismantling

270   plants, especially those handling CRT monitors and TVs, where such items are separated from other WEEE to permit recovery of

271   glass from CRT screens. LODs for both hand-held XRF and LA-ICP-MS fell far below the lowest of the low POP concentration limits

272   (LPCLs) in Annex IV of the POP Regulation for BFRs in plastics (EC No 850/2004); therefore these techniques are capable of

273   addressing current legislation but are also future proofed against further reductions in the maximum concentration levels.

274

275   Given its advantages of speed and relatively low cost, hand-held XRF holds much promise as the method of choice for high

276   throughput monitoring of compliance with legislative limits on BFR concentrations in WEEE. However, although the current limits

277   such as EU directive 2011/65/EU are specified in terms of the concentration of the BFRs, XRF can only measure elemental Br.

278   This presents a practical problem, as for example if limit for PBDEs is 0.1%, then if the XRF reports 0.075% in weight of Br, this

279   equates to 0.090% BDE-209, but 0.106% Penta-BDE. In other words, the limit is exceeded if the Br is due to Penta-BDE but not if

280   it results from the presence of Deca-BDE. A possible practical "work-round" is to specify the limit in terms of Br, but making a

281   conservative assumption that it originates from the presence of a widely used BFR with the lowest proportion of Br, such as

282   Penta-BDE. While doing so will result in some marginal false exceedances of the limit, it will facilitate the widespread use of

283   hand-held XRF to monitor compliance with limit values. Given the enormous mass of WEEE and waste soft furnishings that

284   contain BFRs, the implementation of such an accurate yet rapid and relatively inexpensive monitoring technique is essential, as

285   large-scale application of traditional GC-MS and LC-MS methods appear uneconomic.

286

Acknowledgements

References

295   Petreas M., Oros D., 2009. Polybrominated diphenyl ethers in California wastestreams. Chemosphere 74, 996-1001.

296

297   La Guardia M. J., Hale R. C., Harvey E., 2006. Detailed polybrominated diphenyl ether (PBDE) congener composition of the

298   widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. Environ. Sci. Technol. 40, 6247-6254.

299

300

301   Hale R. C., La Guardia M. J., Harvey E., Gaylor M. O., Mainor, T. M., 2006. Brominated flame retardant concentrations and treads

302   in abiotic media. Chemosphere 64, 181 – 186.

303

304

305   de Wit C. A., Herzke D., Vorkamp K., 2010. Brominated flame retardants in the Arctic environment - trends and new candidates.

306   Sci. Total Environ. 408, 2885-2918.

307

308   Covaci A., Grecke A.C., Law R.J., Voorspoels S., Kohler M., Heeb N.V., Leslie H., Allchin C.R., de Boer J., 2006.

309   Hexabromocyclododecanes (HBCDs) in the environment and humans: A review. Environ. Sci. Technol. 40, 3679–3688.

310

311

312   Samsonek J., Puype, F., 2013. Occurrence of brominated flame retardants in black thermo cups and selected kitchen utensils

313   purchased on the European market. Food. Addit. Contam. 30 (11), 1976-1986.

314

315   Ashton M., Kantai T., Kohler P.M., Roemer-Mahler A. and Templeton J., Summary of the Fourth Conference of the Parties to the

316   Stockholm Convention on Persistent Organic Pollutants, Stockholm, 2009.

317

318   Secretariat of the Stockholm Convention. 2015. Guidance on Best Available Techniques and Best Environmental Practices for

319   the Recycling and Waste Disposal of Articles Containing Polybrominated Diphenyl Ethers (PBDEs) Listed Under the

320   Stockholm   Convention   [Online].   Châtelaine,   Switzerland.   Available   at:

321   http://chm.pops.int/Implementation/NIPs/Guidance/GuidanceonBATBEPfortherecyclingofPBDEs/Tabid/3172/Default.aspx

322   [Accessed: 30 Nov. 2015].

323

324   Schlummer M., Mäurer A., Leitner T. and Spruzina W., 2006. Report: recycling of flame-retarded plastics from waste electric and

325   electronic equipment (WEEE) Waste Manag. Res. 24, 573-583,

326

327   Sakai S., Watanabe J., Honda Y., Takatsuki H., Aoki I., Futamatsu, M., and Shiozaki, K., 2001. Combustion of brominated flame

328   retardants and behavior of its byproducts. Chemosphere 42, 519-531.

329

330   International Electrotechnical Commission (IEC), 2013, IEC62321-3-1:2013. "Determination of Certain Substances in

331   Electrotechnical Products - Part 3-1: Screening Electrotechnical Products for Lead, Mercury, Cadmium, Total Chromium and

332   Total Bromine Using X-ray Fluorescence Spectrometry."

333

334   Regulation (EC) No. 1907/2006 of the European Parliament and of the Council of 18 December 2006 concerning the

335   Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency,

336   amending Directive 199/45/EC and replacing Council Regulation (EEC) No. 793/93 and Commission Regulation (EC) No.

337   1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and

338   2000/21/EC, Off.J.Eur.Commun., 2006, 396,1.

339

340   Kalnicky D.J., Singhvi R., 2001. Field portable XRF analysis of environmental samples. J. Hazard. Mater. 83, 93–122.

341

342   http://chm.pops.int/Implementation/NIPs/Guidance/GuidanceonBATBEPfortherecyclingofPBDEs/Tabid/3172/Default.aspx

343   MacLeod S., International Electrotechnical Commission, Technical Committee 111 "Environmental standardization for electrical

344   and electronic products and systems", Working Group #3 "Test methods of hazardous substances", Greater New York City

345   Area, 2010.

346

347   Košler J. 2008. Laser ablation sampling strategies for concentration and isotope ratio analyses by ICP−MS. In: Sylvester, P., ed.

348   Laser-Ablation-ICP-MS in the Earth Sciences. Newfoundland & Labrador, A1B 3X5: Mineralogical Association of Canada, 6

349   79-88.

350

351   Gallen C., Banks A., Brandsma S., Baduel C., Thai P., Eaglesham, G., Heffernan A., Leonards P., Bainton P., Mueller J.F., 2014.

352   Towards development of a rapid and effective non-destructive testing strategy to identify brominated flame retardants in

353   the plastics of consumer products. Sci. Total Environ. 491-492, 255-65.

354

355   Bart J.C.J., 2001. Direct solid sampling methods for gas chromatographic analysis of polymer/additive formulations. Polym. Test.

356   20, 729-740.

357

358 Persistent Organic Pollutants Review Committee, Technical review of the Implications of Recycling Commercial

359   Pentabromodiphenyl Ether and Commercial Octabromodiphenyl Ether. 6th POP Reviewing Committee meeting, Geneva

360   2010.

361

362 Stehrer T., Heitz J., Pedaring J.D., Huber N., Aeschilmann B., Gunther D., Scherndl H., Linsmeyer T., Wolfmeir H., Arenholz E.,

363   2010. LA-ICP-MS Analysis of Waste Polymer Materials. Anal. Bioanal. Chem. 398, 415-424.

364

365 Mans, C., Simons, C., Hanning, S., Janssen, A., Alber, D., Radtke, M., Reinholz, U., Buehler A., Kreyenschmidt, M., 2009. New

366   polymeric candidate Reference Materials for XRF and LA-ICP-MS - Development and preliminary Characterization. J. XRAY

367   Spectrom. 38, 52-57.

368

369 Jakab, E., Uddin, Md. A., Bhaskar T., Sakata, Y., 2003. Thermal decomposition of flame-retarded high-impact polystyrene. J.

370   Anal. Appl. Pyrolysis. 68-69, 83-99.

371

372 Encyclopedia of polymer science and technology, Wiley, Pittsburgh, 2013, DOI: 10.1002/0471440264.

373

374 Todoli, G.L., Mermet, J.M., 1998. Study of polymer ablation products obtained by ultraviolet laser ablation inductively coupled

375   plasma atomic emission spectrometry. Spectrochim. Acta B- Atomic Spectroscopy. 53, 1645-1656.

376

377 Mans, C., Hanning, S., Simon, C., Wegner, A., Janssen A., Kreyenschmidt, M., 2007. Development of suitable plastic standards for

378   XRF Spectrochim. Acta B: Atomic Spectroscopy. 62B, 116-122.

379

380 Hosaka A., Watanabe C. and Tsuge S., 2005. Rapid determination of decabromodiphenyl ether in polystyrene by thermal

381   desorption-GC/MS. Anal. Sci. 21, 1145-1147.

382

383 Puype F., Samsonek J., Knoop J., Egelkraut-Holtus M., Ortlieb M., 2015. Evidence of waste electrical and electronic equipment

384   (WEEE) relevant substances in polymeric food-contact articles sold on the European market. Food. Addit. Contam. Part A,

385   32, 410-426.

386

387   Puype F., Samsonek J., 2008. Evaluation of the quantitative analysis of PBDEs in plastics by thermal desorption GC-MS for

388   soluble plastics. Organohalogen Compounds. 70,1522–1525.

389

390   Niu J., Shen Z., Yang Z., Long X., Yu G., 2006. Quantitative structure–property relationships on photodegradation of

391   polybrominated diphenyl ethers. Chemosphere. 64, 658-665.

392

393   Guillong M., Horn I., Günther D., 2003. A Comparison of 266 nm, 213 nm and 193 nm produced from a single solid state Nd:YAG

394   laser for Laser Ablation ICP-MS. J. Anal. At. Spectrom. 18, 1224-1230

395

396   Gonzales, J., Mao, X.L., Roy, J., Mao, S.S., Russo, R.E., 2002. Comparison of 193, 213 and 266 nm laser ablation ICP-MS. J. Anal.

397   At. Spectrom. 17, 1108-1113.

398

399   Longerich H. P., Jackson S.E., Gunther D., 1997. Laser-Ablation Inductively Coupled Plasma-Mass Spectrometric transient signal

400   data acquisition and analyte concentration. J. Anal. At. Spectrom. 12, 391-391.

401

402   Danyushevsky L., Robinson, P., Gilbert S., Norman M., Large R., McGoldrick, P., Shelley, M., 2011. Routine quantitative multi-

403   element analysis of sulphide minerals by laser ablation ICP-MS: Standard development and consideration of matrix effects.

404   Geochem.-Explor. Env A. 11, 51-60.

405

406   İzgi B., Kayar M., 2015. Determination of bromine and tin compounds in plastics using laser ablation inductively coupled plasma

407   mass spectrometry (LA-ICP-MS). Talanta, 139, 117-122.

408

409   Evans E. H., Giglio J. J., 1993. Interferences in inductively coupled plasma mass spectrometry. A review. J. Anal. At. Spectrom. 8,

410   1–18.

411

412   Marshall J., Franks J., Abell I., Tye C., 1991. Quantification method for elemental bio-imaging by LA-ICP-MS using metal spiked

413   PMMA films. J. Anal. At. Spectrom. 6, 145-150.

414

415

Table

Table 1 Current limitations of XRF and LA-ICP-MS analysis for the quantification of BFRs in polymers and improvement strategies using the combined XRF, LA-ICP-MS and TD-GC-MS instrumentation for this current study.

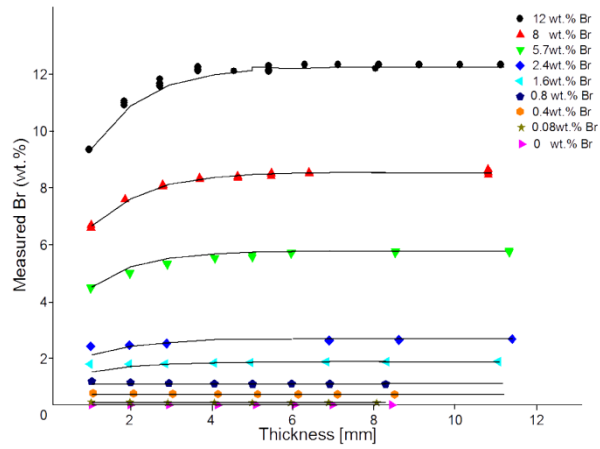| Technique	Specification	Proposed solution/measures applied
XRF	Standard reference material is only available in pellets and only at very low Br concentrations	Use customised reference material containing BFRs at a relevant concentration range. Method evaluation specifically by combining XRF and LA-ICP-MS measurements
	Very thin plastics can give errors: - negative: because the absorption of radiation is dependent on the sample thickness, the sample is too thin as polymeric matrixes are virtually transparent to XRF. No absorbance of secondary emissions is performed by the material itself. - positive: because Br fluorescence might originate from components located beneath the plastic housing (*e.g.* circuit boards)	- develop a thickness calibration to provide a correction equation to account for the influence of polymer thickness on measured Br concentration - samples and standards needs to be measured disassembled from the item and using a lead-lined auto-sampler stand to avoid contamination from beneath the sample
	Br might not come from BFRs: - due to the presence of inorganic Br - Spectral interferences (other elements with similar fluorescence energy, overlapping Br emission lines)	- Br measurements compared with a BFR specific identification method (*i.e.* TD-GC-MS) - Ratio between the two main X-ray fluorescence lines for Br ($K\alpha1$ and $K\beta1$) is used to normalise the most intense line.
	Analysis of plastics with high levels of BFRs display substantial negative error due to self-absorption	Low *and* high concentration level reference materials are used for calibration
LA-ICP-MS	Solid standards that ablate in the same way of the samples for calibration are needed	A set of calibration materials based on ABS containing commonly used additives and fillers were used.
	Difficulty to use internal standards[97]	External calibration was performed with the 9 calibration materials
	Sample inhomogeneity might cause not representative results for Br concentration measurements	Macroscopic homogeneity of reference material was assessed with XRF; microscopic homogeneity was assessed with synchrotron radiation µ-XRF

Figure

Fig. 1 Measured Br concentration by XRF against thickness for different concentration levels of the RMs. Proposed model (equation (2)) for the fitting function (black line).
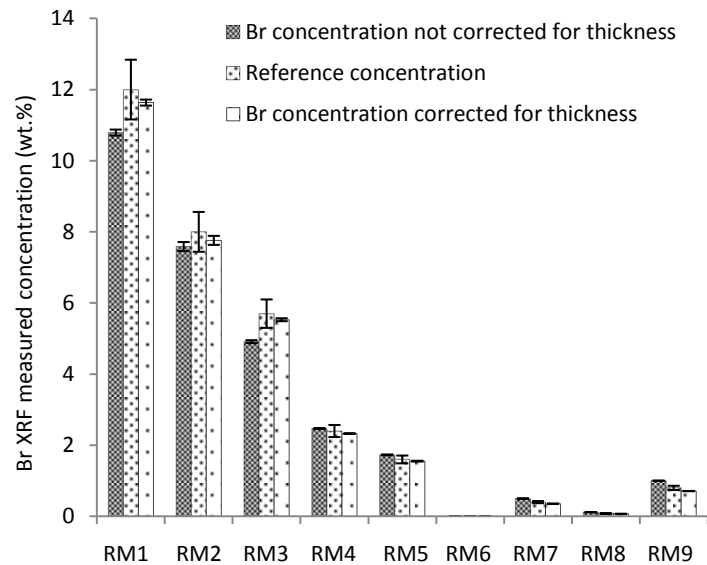
Fig. 2 XRF accuracy was measured comparing the reference value to the corrected values of Br (wt. %) measured at the infinite thickness. Error bars for the measured concentrations are the SD between the 3 replicates done for each measure at infinite thickness; error bars for the reference concentration are uncertainty of the NAA used to validate the RMs. Concentrations reported without correction show negative errors for RM 1-3 and positive errors for RM 4-9: this effect is a direct result of Compton scattering, the Compton scatter intensity increases with the decreasing of the average atomic number of the scattering material, when the Br (Z=80) amount relative to the C in the matrix (Z=12) decreases under a certain threshold the MAC of the material decreased, and the Compton scattering has a more prominent effect . Being this an effect of varying MAC, it is as well accounted for in the thickness correction.
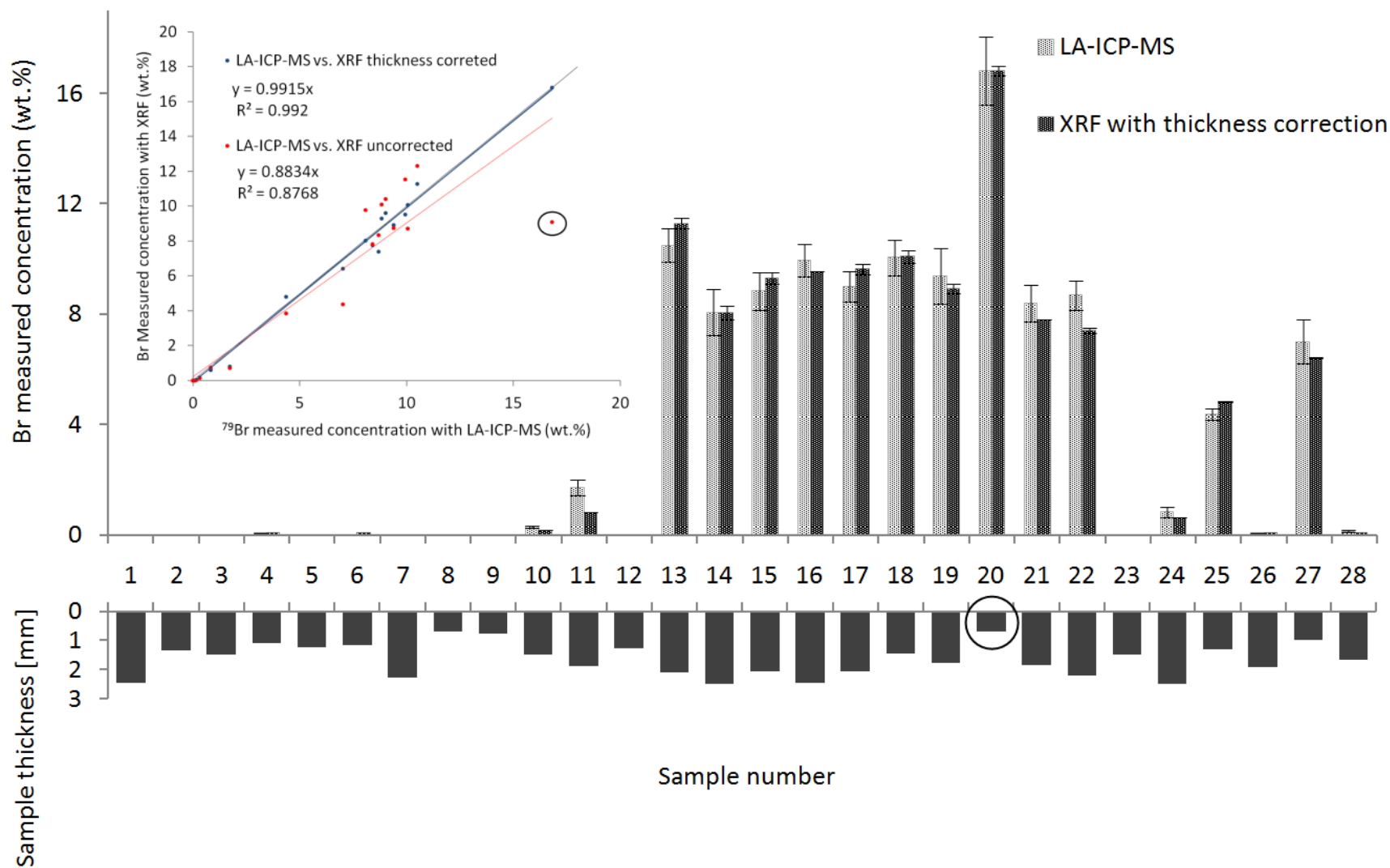
Fig. 3 Comparison between LA-ICP-MS measured values and thickness corrected XRF measured values. On the bottom the corresponding thickness for each sample. Inset plot: correlation between LA-ICP-MS results and XRF. The thickness corrected results (blue dots) show a better correlation (R2=0.9926 for 28 samples) compared to the correlation ((R2=0.8788 for 28 samples) of the non-corrected XRF results (red dots). The

circled red dot (in the inset) shows a bigger deviation from the LA-ICP-MS results: this is in fact a very thin sample (0.69 mm) circled thickness bar, hence when the thickness correction is not applied the negative error is substantially bigger.

Supplementary Material

Improving the accuracy of hand-held X-ray fluorescence spectrometers as a tool for monitoring brominated flame retardants in waste polymers

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An optimised method for Br quantification as a metric of brominated flame retardant (BFR) concentrations present in Waste Electrical and Electronic Equipment (WEEE) polymers is proposed as an alternative to the sophisticated, yet time consuming GC-MS methods currently preferred. A hand-held 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 to perform an external calibration for hand-held XRF ranging from 0.08 to 12 weight % of Br, and 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 here for hand-held XRF and the resulting correction, was applied to 28 real samples and showed excellent (R^2=0.9926) accordance with measurements obtained via LA-ICP-MS. This confirms the validity of hand-held XRF as an accurate technique for the determination of Br in WEEE plastics. This is the first use of solid standards to develop 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 WEEE polymer samples. 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*.

Figure captions

Text

Fig. 1 Measured Br concentration by XRF against thickness for different concentration levels of the RMs. Proposed model (equation (2)) for the fitting function (black line).

Fig. 2 XRF accuracy was measured comparing the reference value to the corrected values of Br (wt. %) measured at the infinite thickness. Error bars for the measured concentrations are the SD between the 3 replicates done for each measure at infinite thickness; error bars for the reference concentration are uncertainty of the NAA used to validate the RMs. Concentrations reported without correction show negative errors for RM 1-3 and positive errors for RM 4-9: this effect is a direct result of Compton scattering, the Compton scatter intensity increases with the decreasing of the average atomic number of the scattering material, when the Br (Z=80) amount relative to the C in the matrix (Z=12) decreases under a certain threshold the MAC of the material decreased, and the Compton scattering has a more prominent effect . Being this an effect of varying MAC, it is as well accounted for in the thickness correction.

Fig. 3 Comparison between LA-ICP-MS measured values and thickness corrected XRF measured values. On the bottom the corresponding thickness for each sample. Inset plot: correlation between LA-ICP-MS results and XRF. The thickness corrected results (blue dots) show a better correlation (R^2=0.9926 for 28 samples) compared to the correlation ((R^2=0.8788 for 28 samples) of the non-corrected XRF results (red dots). The circled red dot (in the inset) shows a bigger deviation from the LA-ICP-MS results: this is in fact a very thin sample (0.69 mm) circled thickness bar, hence when the thickness correction is not applied the negative error is substantially bigger.

Supporting Information

Fig. 1 Effect of thickness on the measured concentration by XRF. All the RMs were measured at different thicknesses, the measured concentration deviates more from the reference for thinner samples.

Fig. 2 a) Effect of high fluence (3.2 J/cm^2) on the ICP-MS signal fluctuations using an ABS reference material (0.8 wt.% Br).

b) Effect of low fluence (0.45 J/cm^2) on the ICP-MS signal fluctuations using an ABS reference material (0.8 wt. %Br).

Fig. 3 Effect of increasing repetition rate on LA-ICP-MS signal intensity (normalized) for RM loaded with 0.8 wt. % Br in a line scan at 50 µm·s^{-1}. Spot size was 150 µm, laser energy was 0.45 J/cm^2. Error bars are the RSDs on the time signal (normalized).

Fig. 4 Number of shots vs. crater depth with LA-ICP-MS. The circles are the values of shots for which the crater depth increases linearly. The linear equation shown in the graphs was used to extrapolate the ablation rate.

Fig. 5 Calibration line on the low concentration range (0.08-0.8 wt.% Br) blue marker and on the high concentration range (1.6-12 wt. % Br) black marker done with LA-ICP-MS.

Fig. 6 Comparison for each RM between the measured value (LA-ICP-MS) and the reference. Error bars for the RMs values is the RSD of the LA-ICP-MS used to measure the Br concentration in the RMs by FMLIA; error bars for the measured concentration is the RSD of the individual ablations.