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Chaine, Cecilia; Hursthouse, Andrew S.; Jandric, Aleksander; McLean, Bruce; McLellan, Iain; McMahon, Brian; McNulty, Jim; Miller, Jan; Salhofer, Stefan; Viza, Evi

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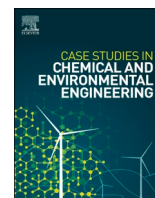
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Case Report

Optimized industrial sorting of WEEE plastics: Development of fast and robust h-XRF technique for hazardous components

Cecilia Chaine^{a,b,*}, Andrew S. Hursthouse^b, Aleksander Jandric^c, Bruce McLean^d, Iain McLellan^b, Brian McMahon^a, Jim McNulty^a, Jan Miller^e, Stefan Salhofer^c, Evi Viza^b^a Restructa Ltd, North Newmoor Industrial Estate, Irvine, KA11 4JU, UK^b School of Computing, Engineering & Physical Sciences, University of the West of Scotland, Paisley, PA1 2BE, UK^c Universität für Bodenkultur Wien (BOKU – University of Natural Resources and Life Sciences, Vienna, Austria^d CCL (North) Ltd, Meadowhead Industrial Estate, Irvine, KA115AU, UK^e School of Health & Life Sciences, University of the West of Scotland, Paisley, PA1 2BE, UK

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ABSTRACT

Waste electrical and electronic equipment (WEEE) are a source of both hazardous and valuable materials that must be segregated for treatment. Previous studies addressing the use of handheld X-Ray fluorescence (h-XRF) as a sorting tool for WEEE plastics through the identification of hazardous components include plastics from mixed WEEE streams, processed material (shredded or treated plastics) and low number of samples not allowing to consider their findings for application on an industrial scale. Thus, further research is needed to establish scalable robust methods for sorting this material. We describe a study carried out on whole flat panel display equipment (FPD) plastic casings using h-XRF for the detection of total bromine (Br) and antimony (Sb) as tracers for Brominated Flame Retardants (BFRs) and Sb₂O₃ additives. The aim being to characterize the targeted material and to define the optimal analysis conditions to meet large scale throughputs. A ring trial exercise comprising 100 samples was conducted to evaluate the validity of the measurements. Results indicate that: 1) the use of h-XRF under the conditions determined in this study offers a valid technique to screen total Br and Sb in whole FPD casings at industrial scale with low uncertainty, 2) Br and Sb are found to be homogeneously distributed within the casing, 3) an optimal h-XRF analysis time of 10 seconds is suitable from both accuracy and practical implementation for LOD<[Br]≤ 830 mg kg⁻¹ and LOD<[Sb]≤8400 mg kg⁻¹, and 4) the presence of dust deposited on the casings was excluded as a factor affecting h-XRF results. To our knowledge this is the first evaluation of optimal sorting conditions for whole display casings using h-XRF, within a manual dismantling process.

1. Introduction

Waste electrical and electronic equipment is the fastest growing waste stream worldwide. According to reports published in 2020, 11.8 Mt were generated between 2014 and 2019 and considering the projected annual growth rate of 2 Mt, WEEE volumes could exceed 74 Mt by 2030 [1].

The priority characteristic of WEEE is the presence of potentially toxic chemical compounds which makes it hazardous waste. Including a wide variety of materials such as ferrous and non-ferrous metals, plastics

account for approximately 30% of the volume of WEEE generated annually, comprising a wide variety of polymers. ABS (Acrylonitrile Butadiene Styrene), HIPS (High Impact Polystyrene), PC + ABS (Polycarbonate + Acrylonitrile Butadiene Styrene) and PPE (Polyphenyl Ether) are the most frequently found [2].

As a consequence of this diversity, sorting plastic is complex resulting in low recycling rates with estimates suggesting that between 40 and 50% of recovered volumes are not being adequately recycled [3]. Adding to this challenge is the presence of certain additives such as flame retardants, which, if not treated properly, may be released from the polymer matrix as primary pollutants [4,5] or function as catalysts

* Corresponding author. School of Computing, Engineering & Physical Sciences, University of the West of Scotland, Paisley, PA1 2BE, UK.

E-mail addresses: cecilia.chaine@uws.ac.uk (C. Chaine), andrew.hursthouse@uws.ac.uk (A.S. Hursthouse), aleksander.jandric@boku.ac.at (A. Jandric), bruce@cclnorth.com (B. McLean), iain.mclellan@uws.ac.uk (I. McLellan), brian.mcmahon@restructa.co.uk (B. McMahon), jim.mcnulty@restructa.co.uk (J. McNulty), jan.miller@uws.ac.uk (J. Miller), stefan.salhofer@boku.ac.at (S. Salhofer), evi.viza@uws.ac.uk (E. Viza).

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Abbreviations

WEEE	Waste of Electrical and Electronic Equipment
FPD	Flat Panel Display Equipment
h-XRF	Handheld X-Ray Fluorescence
BFR	Brominated Flame Retardants
LOD	Limit of Detection
LOQ	Limit of Quantification
ABS	Acrylonitrile Butadiene Styrene
HIPS	High Impact Polystyrene
PC + ABS	Polycarbonate + Acrylonitrile Butadiene Styrene
PPE	Polyphenyl Ether
PBDEs	Polybrominated Diphenyl Ethers

TBBPA	Tetrabromobisphenol A
HBB	hexabromobiphenyl
HBCDD	hexabromocyclododecane
POPs	Persistent Organic Pollutants
GHS	Globally Harmonized System
EU	European Union
UK	United Kingdom
AATF	Approved Authorised Treatment Facilities
GC/MS	Gas Chromatography/Mass Spectrometry
ICP/OES	Inductively coupled plasma atomic emission spectroscopy
CRM	Certified Reference Material
CRT	Cathode Ray Tube

for a variety of different dioxins and furans and therefore have a significant impact on health and the environment as secondary pollutants [6].

According to an early study by Dawson and Landry, 2005 [7] TV-related fires are identified amongst the most frequent during electrical and electronic equipment (EEE) use, with the introduction of flame retardants resulting in a significant reduction of these incidents. Deca-BDE (Decabromodiphenyl ether), EBP (ethane 1,2 bis (pentabromophenyl)) and EBTBP (ethylene 1,2 bis (tetrabromo phthalimide) EBP) were identified as the most commonly used BFRs. Two years later, Herat, 2008 [8] presented an analysis on the use of BFRs in EEE, reporting in addition to the above, the presence of TBBPA (Tetrabromobisphenol A), HBCDD (Hexabromocyclododecane) and octa-BDE (Octabromodiphenyl ether).

Regulations have been imposed with the aim of reducing the use of these and other BFRs in EEE plastics. For instance, since 2004 and 2008 the use of octa-BDE and deca-BDE respectively, was banned. However, Schlummer et al., 2007 [9] reported only a slight decrease in the fraction of materials containing BFRs compared to that reported for the year 2000 by Leisewitz et al., 2001 [10]. More recent studies indicate that the content of BFRs depends on the type of plastic analysed. Peeters et al., 2014 [11] reported that HIPS and ABS EEE housings generally contain BFRs and only 8.5–14% contain phosphorous flame retardants and/or other additives. Furthermore, a study by Gripon et al., 2021 [12] focusing on ABS shows significant concentrations of TBBPA were found in 88% of the plastics analysed and PBDEs (polybrominated diphenyl ethers) were identified in 11% of the samples with the highest concentrations corresponding to deca/octa/hepta-BDE. In addition, Zhan et al., 2019 [13] observed that the use of BTBPE (1,2-bis(2,4,5-tribromophenoxy)ethane)) as a substitute for traditional BFRs was increasing despite evidence of its similar characteristics to legacy BFRs including its persistence in the environment and potential for bioaccumulation.

PBDEs, HBB (hexabromobenzene) and HBCDDs are included in the Stockholm Convention on Persistent Organic Pollutants (POPs). In 2019, Directive EU 2019/1021 [14] was enforced in Europe to implement the limits set in the Convention. It was then decided that if the sum of PBDEs and/or the sum of HBCDDs exceeds 1,000 mg kg⁻¹ in waste material, it must be classified as POPs waste and treated so that POPs are either destroyed or irreversibly transformed. TBBPA, currently the most extensively applied BFR worldwide, has yet to be declared a POP but the Globally Harmonized System (GHS) classifies it as H410: “very toxic to aquatic life with long lasting effects”. In June 2017, the European Union amended Annex III of Directive 2008/98/EC (Waste Framework Directive) [15], regarding classification of waste as hazardous, setting concentration thresholds for waste containing substances declared as HP14 “Ecotoxic” in the GHS. According to this amendment, WEEE containing TBBPA in a concentration higher than 1,000 mg kg⁻¹ is to be labelled as hazardous and their recycling is forbidden [16]. In the UK, the legal and administrative requirements defined by the Convention are enforced by

the POPs Regulation 2007 [17]. To date, this regulation applies requirements defined in EU 2019/1021 therefore transferring identical concentration limits.

BFRs are usually used in combination with antimony trioxide (Sb₂O₃) as synergist typically found in TV/Display equipment in concentrations of approximately 33–55% of the Br content [18]. In the European Union (EU) and the UK, any waste containing Sb₂O₃ in concentrations higher than 0.1% w/w (10,000 mg kg⁻¹), is to be classified as hazardous under the Chemical Classification, Labelling and Packaging (European Regulation (EC) No 1272/2008) [19].

As a consequence of these regulatory requirements, the WEEE management sector faces the challenge of managing plastics in an environmentally sound and legally compliant manner, while minimising the impact on business profitability. In the UK there are currently no systems in place to promote co-operation between producers, retailers and recyclers within which information on the substances contained in the different components is disclosed. Therefore, in order to improve the efficiency of plastic sorting processes and its recycling rates, it is necessary to develop a technique by which recyclable and non-recyclable plastics are reliably identified and separated, ensuring the correct management of the hazardous fraction. Current state of the art of WEEE plastics management is described in Chaîne et al., 2022 [20].

Different techniques have been studied for the characterisation of BFRs and Sb₂O₃ in WEEE plastics. For measuring BFRs reliable methods include gas chromatography with electron capture detection or mass spectrometry as well as liquid chromatography with different coupled detectors [13,21–23]. On the other hand, the method generally used for the determination of Sb₂O₃ is the analysis by ICP/OES after Sb chemical extraction from the matrix. Considering this compound as the only source of Sb present in WEEE plastics, all the Sb measured is attributed to it.

These conventional methods to determine compliance regulation are technically and economically demanding, with analysis times incompatible with the throughput required at industrial level. For this reason, during the past decade research has increasingly focused on more practical alternatives such X-Ray Fluorescence (XRF) as a fast, non-destructive and effective technique, by which it is possible to rapidly determine total concentrations of Br and Sb as tracers of BFRs and Sb₂O₃ [24,25].

The current global regulatory and economic frameworks, demand for the development and application of cost-effective methods for the identification and sorting of WEEE plastics. Extensive research has been carried out on the application of handheld XRF (h-XRF), however, the results presented do not evaluate the potential of the methodology for its industrial use or are not specifically applicable to all WEEE streams. Assessed matrixes include varied mixes of plastics from different products [18,26], low number of samples [23,27–31] and in many cases samples are collected after shredding [32] or recycling [33]. Thus, it is still necessary to evaluate its application on a larger scale in order to

meet industry processing requirements. For this, it is essential to thoroughly characterize the targeted materials as recovered after disassembling and define the best analysis conditions with an emphasis in reducing analysis times to an optimal minimum to maximize process efficiency without compromising results.

Addressing this we present the development and validation of a technique for sorting whole Flat Panel Display Equipment (FPD) plastic housing using h-XRF. Samples were taken directly from the manual dismantling line at a recycling site located in the UK. The total concentration of Br and Sb in each sample was determined by two parallel analyses of 100 samples using h-XRF carried out at the base company and the University of Natural Resources and Life Sciences, Vienna (BOKU). In addition, 10 samples were analysed for identification of specific BFRs by Gas Chromatography/Mass Spectrometry (GC/MS) at the University of Birmingham and the determination of total Sb was performed by Inductively Coupled Plasma/Optical Emission Spectroscopy (ICP/OES) at the University of the West of Scotland.

2. Materials and methods

Br and Sb measurements carried out at the base company were made using the VANTA™ X-Ray Fluorescence Analyser – C Series with rhodium (Rh) anode tube, supplied by Olympus UK, set on RoHS method. The h-XRF analyser was placed on a stand and remotely operated using the Vanta™ Desktop App placing the window of the analyser directly on the surface of the sample. This allowed for triplicate analysis of each area to be performed without moving the analyser generating consistent replicates.

2.1. Sample conditions

In WEEE manual dismantling facilities dust build up is significant, and in particular in CRT dismantling processes it is likely to contain trace levels of lead (Pb) [34–37].

To determine whether the presence of dust settled on the casings has an impact on h-XRF results, 40 samples (20 front and 20 back casings) were randomly selected from the dismantling process and analysed using $t_{\text{analysis}} = 30\text{s}$. Casings were placed on a stand leaving a gap of approximately 6cm of air behind the analysed area. The surface of the table was cleaned with a lint free cloth dumped in isopropanol at the start and end of the workday. Fig. 1 shows the layout of sample analysis on site.

Each sample was analysed in two different marked areas where dust was most noticeable according to subjective judgement of the analyst. After completing the first analyses dust was removed using a lint-free electrostatic cloth, and the marked areas re-analysed three times under the same h-XRF operation conditions.

2.2. Optimal analysis time

In the use of XRF as a waste screening tool for compliance with regulatory requirements, it is of utmost importance to define the optimum analysis time as it directly correlates to the results accuracy. Several studies have assessed this parameter for Br determination with analysis times ranging from 10 minutes [26] to as low as 1 second [28]. In a study by Aldrian et al., 2015 [21] applied on similar conditions to the present study analysis times between 5 and 30s were evaluated. As for Sb measurements, Turner and Filella, 2017 [38] report the application of analysis times between 60 and 200s in a study on plastics in consumer products. All studies conclude that longer analysis time yield lower relative errors. However, there is no consensus on the times defined as optimal.

Our methodology for determining the optimal analysis time comprised of two stages as described below.



Fig. 1. 23" FPD plastic casing being analysed by the remotely operated VANTA™ handheld XRF Analyser (W: 8.3cm, L: 23.3cm, H:28.9 cm).

2.2.1. Stage 1. optimal analysis time determined on certified reference material

As certified reference material three discs of 1mm, 2mm and 6mm thickness of BAM-H010/ABS were used. Each disc was measured to determine total bromine concentration. Three different analysis times were used: $t = 10\text{s}$, $t = 20\text{s}$, $t = 30\text{s}$; 20 analyses were done for each analysis time. The discs were placed on a stand as depicted in Fig. 2 allowing to have 6cm of air behind them. These conditions were chosen as they would be most representative of those under which whole plastic casing measurements are done. The position of the disc was changed in between analyses to ensure that the same area was not analysed two consecutive times. Certificate for BAM-H010 indicates the bromine concentration to be $(240 \pm 21) \text{mg.kg}^{-1}$.

2.2.2. Stage 2. optimal analysis time determined on plastic samples

Samples were taken from twelve different FPD rear casings including different polymer types: ABS, HIPS, PC + ABS and PS. From each casing four/five subsamples were extracted as discs of 6cm of diameter. Each sub-sample corresponds to a different area (Fig. 3): Top Right (TR), Bottom Right (BR), Top Left (TL), Bottom Left (BL) and Centre(C).

The subsamples were placed on the stand (see Fig. 2) for their analysis using the following times: 50s, 30s, 20s, 15s and 10s; 20 analyses were done for each analysis time.

2.3. FPD plastic casings characterisation: assessing Br and Sb homogeneity

To determine the homogeneity of Br and Sb concentrations in a

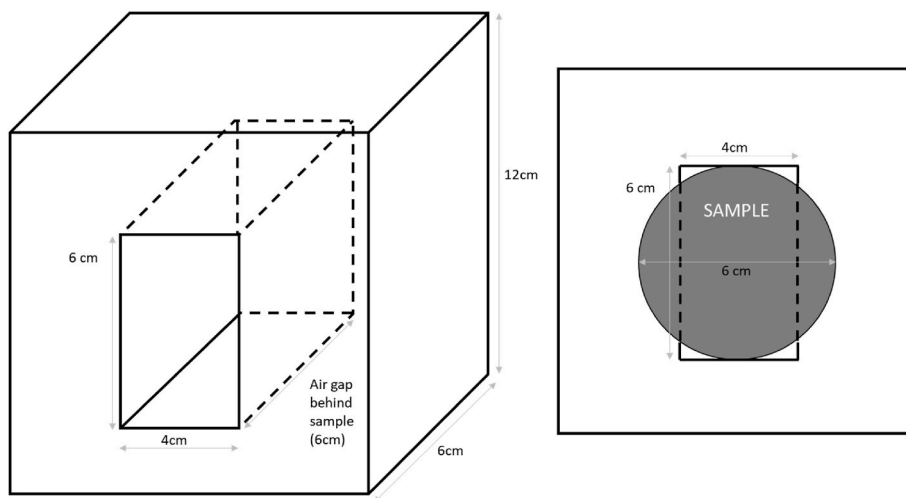


Fig. 2. Diagram of sample stand for XRF analysis.



Fig. 3. Diagram indicating sampled areas on FPD rear casing.

casing, and within a FPD by comparing results for front and rear casings of the same item, sixty-eight samples (68 front and 68 rear casings) were analysed at 9 different areas: Top left, Top right, Bottom left, Bottom right, Centre on rear casings, and Top left, Top right, Bottom left, Bottom right on front casings.

The analyser was placed on the external surface of the sample in all cases, assuming the plastic to be a consistent thickness. Each individual area was measured in triplicate to ensure the reproducibility of the measurement for $t_{\text{analysis}} = 10\text{s}$.

2.4. Validation of h-XRF results

For validation of Br measurements 100 samples previously analysed on site were sent to the Universität für Bodenkultur Wien (BOKU – University of Natural Resources and Life Sciences, Vienna) for their analysis with h-XRF using a different technique. Details are described below.

2.4.1. Technique 1: industry grade h-XRF analysis (on site)

XRF analysis were conducted as described in Section 2.

To build a reference curve for Br two granulated CRMs (EC680 and EC681) and a disc CRM made of ABS (BAM-H010) were used.

2.4.2. Technique 2: laboratory grade h-XRF analysis (BOKU)

Samples were analysed for total Br content using laboratory-grade

conditions by sample-specific h-XRF device calibration. First, the individual samples were placed in an h-XRF measurement chamber for consistency and to increase the reproducibility of the measurements. Each sample was analysed in triplicate using a Soil mode of h-XRF spectrometer (XL3T950, Thermo Scientific Portable Analytical Instruments Inc., Tewksbury, USA). The analyser is equipped with a gold anode and measures at a maximum voltage of 50 kV and a maximum current of 100 μA .

The optimal measurement time for h-XRF is sample-specific and must therefore be determined empirically by evaluating the spectral peaks for the target elements [28]. The maximum Br K α 1 peak at 11.92 keV saturation was reached after $t_{\text{measurement}} = 32\text{s}$ therefore the measurement time was set at 35s.

2.5. Identification of individual Brominated Flame Retardants

XRF is a reliable method that does not require extensive and destructive sample preparation and is faster and less expensive than GC/MS. However, it only allows to determine total element concentration which is not a problem for Sb_2O_3 measurements as it is assumed all Sb comes from it. However, for Br there is not a straightforward relation between its total concentration and the brominated compounds found in the polymer. To characterize these compounds 10 samples were sent to the University of Birmingham for the identification and quantification by GC/MS of PBDEs, HBCDDs and TBBPA, considered to be the most frequently found BFRs in WEEE plastics [3,28,31,33]. Details on the analysis methodology are presented in Drage et al., 2022 [31].

2.6. Sb determination by ICP/OES

Total Sb content was determined in 12 plastic samples by ICP/OES (PerkinElmer Avio500) after acid digestion. Three aliquots of 0.25g of plastic were accurately weighed and each transferred into a Teflon tube to which 3mL of H_2SO_4 (95%) were added. The tubes were placed in a hot block and the temperature was initially increased from room temperature ($\sim 19^\circ\text{C}$) to 120°C in 40 min and maintained for 30 min. Next, 3mL of HNO_3 (69%) and 1mL of H_2O_2 (30%) were added to the sample and held at 120°C for another 120 min. The digested solution was filtered through filter paper 0.45 μm and collected in a 50mL volumetric flask. Solids retained in the filter were dried for 18 hours at 40°C and subjected to a second round of the same acid digestion process. Both digestion products were collected in the same flask and brought to volume with deionized water. To ensure total removal of solids that could interfere with ICP operation, the final solutions were filtered twice through filter paper or syringe filters 0.45 μm .

2.7. Quality assurance/quality control

Total Br and Sb measurements carried out on site were done using a h-XRF analyser calibrated by the manufacturer using suitable reference materials before the start of the study. During the study a daily check was performed at the beginning of each day by measuring in triplicate two Certified Reference Materials (CRM): EC680 m and EC681 m. Control charts were kept to identify deviations in the operation of the equipment or errors associated with the analyst. All values were found to be within the $\pm 3\sigma$ control limits and no systematic patterns were observed, indicating the process to be under control.

Total Br concentrations measured by h-XRF at BOKU were determined based on the calibration curve derived from a Certified Reference Material BAM-H010 (Bundesanstalt für Materialforschung und -prüfung, Germany) provided in 6 different 1 mm thick ABS discs. The total material composition of the BAM-H010 Certified Reference Material (CRM) discs is shown in Table 1.

According to the information from the manufacturer, the BAM-H010 CRM is intended to be used as an analytical control, calibration, or recalibration sample for XRF analysis. Each disc was measured in quintuplet and based on the mean values of fluorescence intensity at the $K\alpha 1$ peak of Br for different concentrations, a calibration curve was calculated using a linear regression model (see Fig. 4).

For BFR analysis, quality assurance and control is described in Drage et al., 2022 [31].

For ICP/OES analysis, a 28 multi-element standard (Fisher Scientific, UK) was used for calibration. Additionally, a blank containing 3mL of H_2SO_4 (95%), 3mL of HNO_3 (69%) and 1mL of H_2O_2 was subjected to the digestion process described in Section 2.6. No Sb was found above the detection limits in this blank therefore results were not corrected for residues.

3. Results and discussion

3.1. Sample conditions

To determine the variation of Pb, Br and Sb concentrations after dusting, the median was calculated for each analysed point. The variation in concentration was determined as:

$$\% \text{ variation} = \left(\frac{\text{Median concentration, dusty} - \text{Median concentration, clean}}{\text{Median concentration, dusty}} \right) \times 100 \quad (1)$$

Negative values of %variation indicate a decrease in the concentration of the element after cleaning. Positive values indicate an increase of the same parameter.

Results for the 20 samples analysed are presented in Fig. 5, showing the element concentration variation for Pb, Br and Sb.

The low percentage of analysis points which presented an increase in Pb concentration is likely explained by cross contamination with the cleaning cloth or dust build-up on the analyser's plastic window.

A decrease in Br concentrations after cleaning was only observed in

Table 1

Overview of six Certified Reference Material 1mm thick ABS plates containing RoHS regulated elements in different concentrations (BAM-H010).

BAM designation	Br concentration (mg.kg^{-1})	
	Mean	Method error
ABS-6	6	0.42
ABS-8	19	1.33
ABS-5	25	1.75
ABS-3	50	3.5
ABS-7	466	32.62
ABS-4	938	65.66

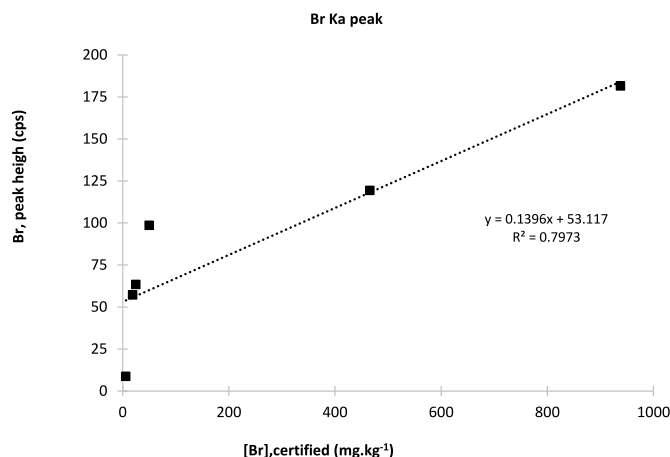


Fig. 4. Calibration curve based on six BAM-H010 1mm ABS discs.

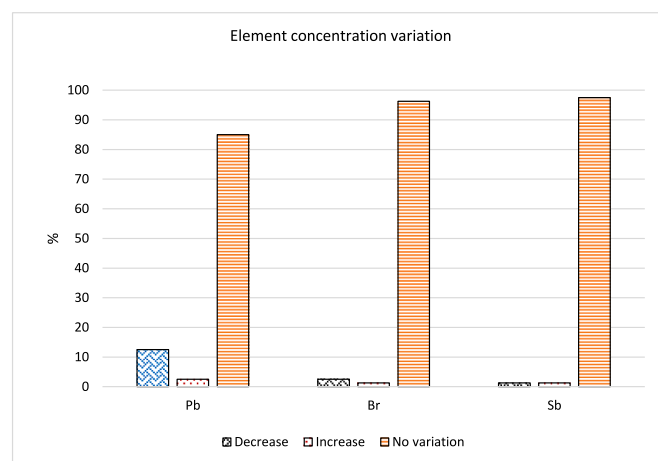


Fig. 5. Element concentration percentile variation comparing Dusty vs. Clean conditions.

~2.5% of the samples. Such a low value suggests that under the conditions used, the presence of dust does not significantly affect Br readings. Sb showed a behaviour relative to that of Br, consistent with previous knowledge of its association with BFRs [18,23].

3.2. Optimal analysis time

3.2.1. Stage 1. optimal analysis time determined on certified reference material

The optimal analysis time was determined by comparing %Accuracy (%) (Equation (2)) for each of the discs at each analysis time.

Equation 2

$$\% \text{ Accuracy} (\%) = \frac{[Br]_{\text{reference}} - ([Br]_{\text{measured}} - [Br]_{\text{reference}})}{[Br]_{\text{reference}}} \times 100 \quad (2)$$

A %Accuracy level of 90% was defined as acceptable for the application of this technique at an industrial scale. To define this, we analysed the impact of these acceptance levels on measurements for over 5,000 samples and concluded it would result in a sorting error of 0.4% (1 item every 250 could potentially be misclassified as recyclable).

For $t = 10$ s, the %Accuracy was estimated to be between 94.6% and 97.0%, depending on the thickness of the sample. Detailed results are presented in Fig. 6.

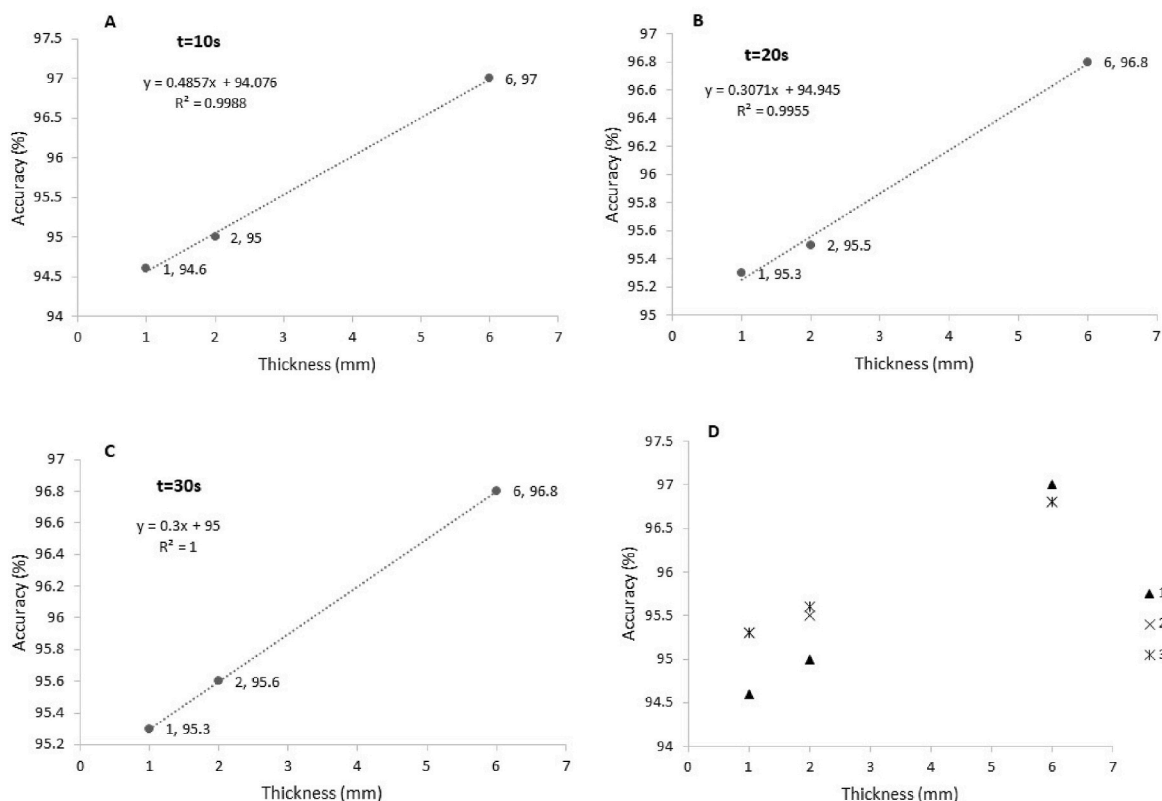


Fig. 6. A) Accuracy of Br concentration determined by XRF in CRM vs. Thickness for an analysis time of 10 seconds, B) Accuracy of Br concentration determined by XRF in CRM vs. Thickness for an analysis time of 20 seconds, C) Accuracy of Br concentration determined by XRF in CRM vs. Thickness for an analysis time of 30 seconds, D) Compiled results for $t = 10s$, $20s$ and $30s$.

3.2.2. Stage 2. optimal analysis time determined on plastic samples

Based on Jandric et al., 2020 [28], results for $t = 50s$ were considered as reference when calculating the %Accuracy by Equation (2).

The %Accuracy for $t = 10s$ is above 99% for Br, while for Sb percentages vary significantly between 84% for $[Sb] \sim 100 \text{ mg kg}^{-1}$ to 99% for $[Sb] \sim 10,000 \text{ mg kg}^{-1}$. As an increase is observed with concentration and the range of interest is $\sim 8,400 \text{ mg kg}^{-1}$, the %Accuracy level was considered to be approximately 99%. Detailed results are presented in Fig. 7.

An analysis time of 10s was determined to be optimal within the following concentration ranges: $LOD < [Br] < 3,500 \text{ mg kg}^{-1}$ and $LOD < [Sb] < 10,000 \text{ mg kg}^{-1}$.

3.3. FPD plastic casings characterisation: assessing Br and Sb homogeneity

Each area was measured in triplicate to ensure the reproducibility of the measurement for $t_{\text{analysis}} = 10s$, considering 95% an acceptable percentual variation. Results were assessed to determine homogeneity of Br and Sb concentrations within each casing and item, and to identify if there was an area with consistently higher concentrations that could be taken as reference for sorting. Concentrations were determined by calculating the median of the three analysis results. The highest concentrations were most frequently found on the Bottom Left area in front casings, and on the Centre area in rear casing. Results are presented in Table 2.

3.4. Validation of h-XRF results: ring trial

The reference curve obtained for Technique 1 and the Calibration curve for Technique 2 are presented in Fig. 8. To assess the correlation between both methods, we compared their results sets (Fig. 9 & Table 3)

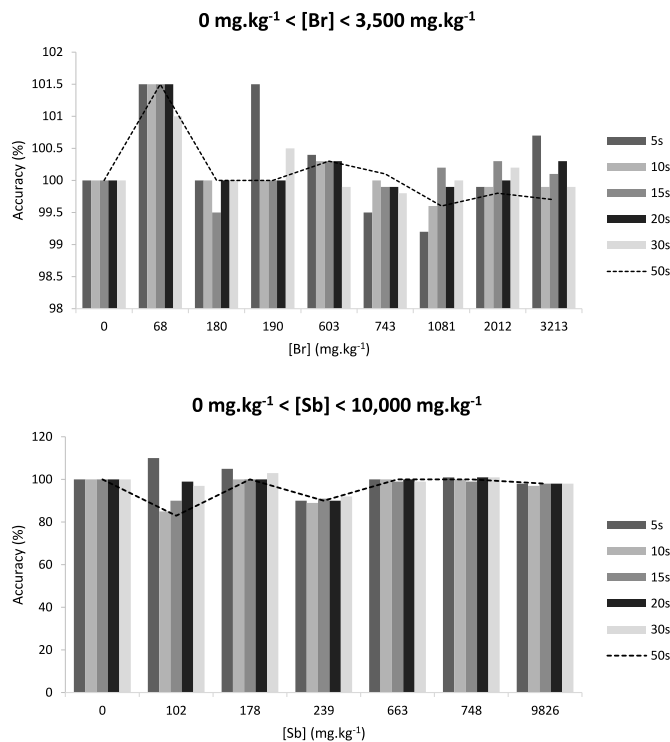


Fig. 7. Calculated Accuracy (%) vs Elemental concentration for Br and Sb (mg.kg^{-1}) according to concentration range.

Table 2

Frequency of highest Br & Sb concentrations per area analysed in Front and Rear FPD casings.

	Area	Frequency (%)
FRONT CASING	Bottom Left	55.9
	Bottom Right	17.6
	Top Right	14.7
	Top Left	11.8
REAR CASING	Centre	60.3
	Bottom Right	11.8
	Bottom Left	10.3
	Top Left	8.8
	Top Right	8.8

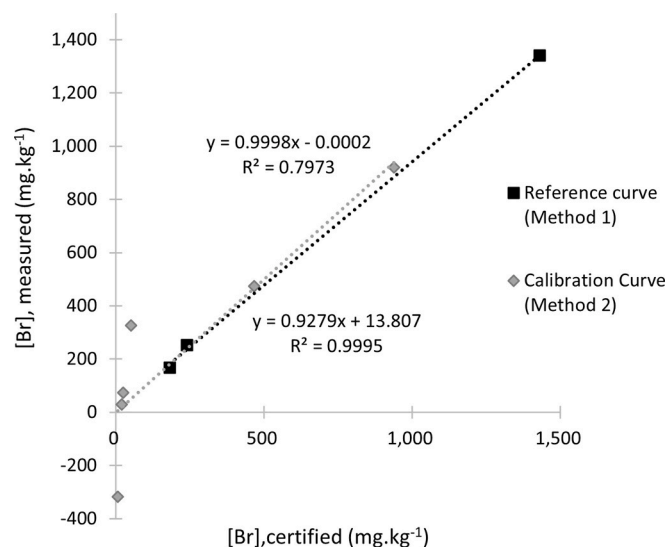


Fig. 8. Reference curve for method 1. Calibration curve for method 2 (see Section 2.4).

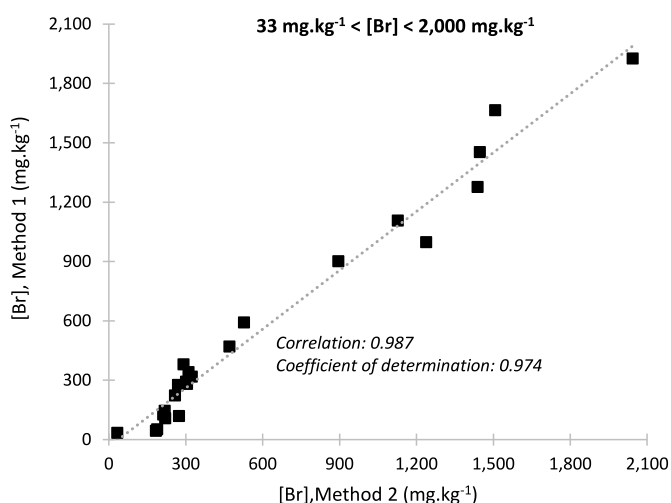


Fig. 9. [Br] measured by Technique 2 vs. [Br] measured by Technique 1.

and did a Pearson's test. Results indicate there is a strong positive linear correlation between Br concentrations measured by Technique 1 and Technique 2 for the same group of samples in the range $LOD < [Br] < 2,000 \text{ mg kg}^{-1}$

We performed additional statistical analysis to further evaluate the correlation between the two methods. First, we evaluated the normality of the distribution of the results for each method by doing a Shapiro-

Table 3

[Br] measured by Technique 1 & Technique 2 for samples with measured [Br] between 33 mg kg^{-1} and $2,000 \text{ mg kg}^{-1}$.

ID	Polymer	[Br] (mg.kg^{-1}) Technique 1	[Br] (mg.kg^{-1}) Technique 2
1	HIPS	33	33
2	HIPS	184	44
3	HIPS	190	51
4	ABS	220	107
5	ABS	274	118
6	ABS	213	126
7	HIPS	219	145
8	PC + ABS	259	223
9	ABS + PET	271	276
10	ABS	306	281
11	PPE + SB	301	292
12	HIPS	325	318
13	HIPS	311	340
14	HIPS	292	380
15	ABS	471	470
16	HIPS	528	591
17	HIPS	896	901
18	ABS	1,238	997
19	HIPS	1,128	1,107
20	ABS	1,439	1,276
21	HIPS	1,448	1,453
22	HIPS	1,508	1,665
23	HIPS	2,044	1,925

Wilk test and assessing the corresponding Q-Q plots. The following hypotheses were considered: H_0) The variable extracted from the sample follows a normal distribution, H_a) The variable extracted from the sample does not follow a normal distribution. Results are presented below (Table 4 and Fig. 10).

As the computed p-value is lower than the significance level $\alpha = 0.05$, one should reject the null hypothesis H_0 , and accept the alternative hypothesis, H_a . Results from Techniques 1 and 2 do not follow a normal distribution.

To determine whether the results follow the same distribution we did a Wilcoxon signed-rank test (two-tailed). We obtained a p-value of 0.039, lower than the significance level $\alpha = 0.05$, therefore we rejected the null hypothesis and accepted that the distribution of the two datasets are different. For this test samples with results $< LOD / < LOQ$ (see Section 3.4.1) were not considered for the statistical analysis.

As the measurements by either method imply a certain degree of error which we are not able to quantify, neither of the methods provides an unequivocally correct measurement, so we assessed the degree of agreement between them by doing a Deming regression test and a Bland & Altman test [39].

3.4.1. Limit of detection/limit of quantification (LOD/LOQ)

Technique 1: The analyser manufacturer reports a LOD of 1 mg kg^{-1} and 2 mg kg^{-1} for Br and Sb respectively, for two polymeric matrixes: PE (polyethylene) and PVC (Polyvinyl chloride) based on automatically selected beam conditions and an analysis time of 60 seconds [40]. No other reports were found for studies using the Olympus VANTA™ h-XRF analyser, therefore for our measurements those limits were considered:

$$LOD, Br = 1 \text{ mg kg}^{-1} / LOQ^*, Br = 3 \text{ mg kg}^{-1}$$

$$LOD, Sb = 2 \text{ mg kg}^{-1} / LOQ^*, Sb = 6 \text{ mg kg}^{-1}$$

Table 4

Shapiro Wilk test results for Techniques 1 & 2.

Shapiro-Wilk test	Technique 1	Technique 2
W	0.786	0.834
p-value (2-tailed)	0.000	0.001
α	0.05	0.05

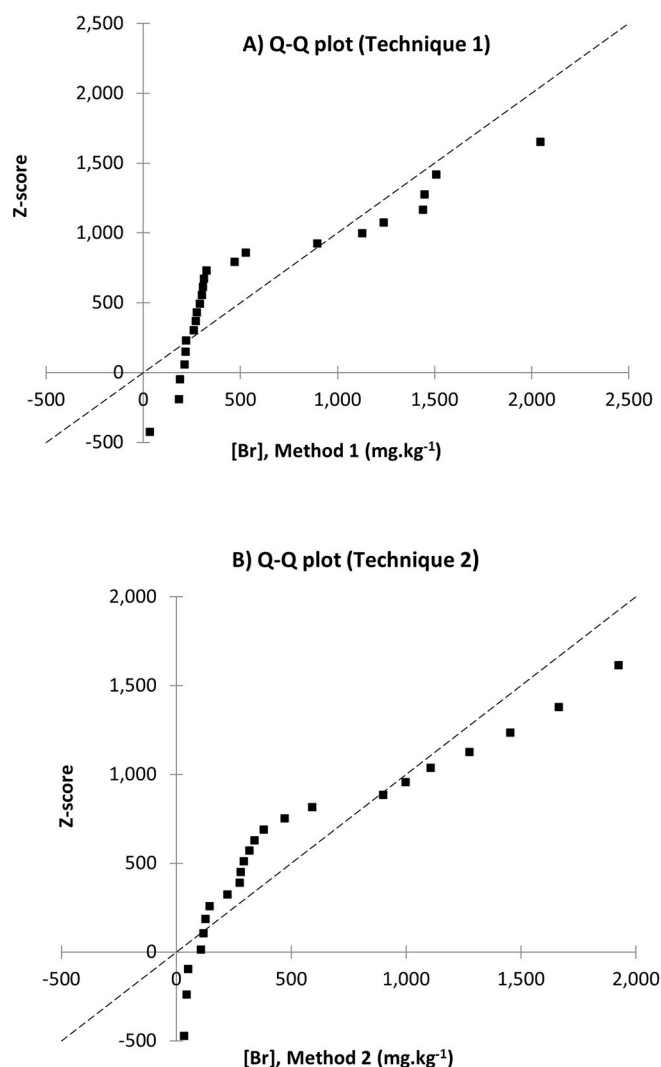


Fig. 10. Qq plots: A. Technique 1, b. Technique 2.

*The limit of quantification was calculated as $3.3 \times \text{LOD}$ [41].

Technique 2: To define the signal detection limit (S_{dl}), the following formula was used (see Equation (3)), while the limit of quantification was calculated as $3.3 \times S_{dl}$ [41].

Equation (3). Signal detection limit formula

$$S_{dl} = S_{reag} + 3\sigma_{reag}$$

$$S_{dl} = 5.45 + 3 \times 0.52 = 7.01 \text{ cps} - 10 \text{ mg kg}^{-1} \quad (3)$$

S_{reag} : Signal mean value of the blank sample; σ_{reag} : Standard deviation of the blank signal

$$\text{LOQ} = 10 \text{ ppm} * 3.3 = 33 \text{ ppm}$$

Table 5
Deming regression results.

	Value	Lower bound 95% (Mean)	Upper bound 95% (Mean)
Intercept	45.160	-5.944	96.263
Slope coefficient	0.995	0.892	1.099

3.4.2. Deming regression test results

Results are presented in Table 5 and Fig. 11 below.

The value of the intercept is 45.160, and its confidence interval includes the value 0. This value measures whether the systematic difference of the two techniques is equal to 0. The slope coefficient is equal to 0.995, and the confidence interval includes the value 1. This means that the proportional difference between the two techniques is equal to 1.

We can confirm there are no systematic differences or proportional differences between both techniques.

3.4.3. Bland & Altman test results

Hypotheses considered were: Ho) The difference between the means is equal to 0, Ha) The difference between the means is different from 0. Results are presented in Table 6 and Fig. 12.

As the computed p-value is lower than the significance level $\alpha = 0.05$, we accept the alternative hypothesis Ha. The mean difference (Bias) is -42.504 , meaning that on average Technique 1 measures $42.504 \text{ mg kg}^{-1}$ more than Technique 2. Since we do not know the true value of the Br concentration for each sample, the mean of the two measurements is the best estimate.

The visual examination of the plots (Fig. 12) provides an assessment of the global agreement between both measurements. The histogram shows the differences are normally distributed. This was verified by a Shapiro-Wilk test. Therefore, we could expect 95% of the differences to lie between $\pm 1.96\sigma$ limits of agreement. Thus, results measured by Technique 2 may be 138 mg kg^{-1} above or 223 mg kg^{-1} below those of Technique 1.

The limits of agreement are too wide to define the techniques as equivalent. However, considering $[\text{Br}] < 830 \text{ mg kg}^{-1}$ as a concentration threshold to sort POP plastics, all samples would have been classified under the same categories independent of the technique used. It must also be considered that the calibration curve for Technique 2 has a relatively low r^2 value although it was determined using a certified reference material made of a polymer found in our samples (ABS) and comprises 6 points including a blank. Conversely, for Technique 1 the used reference curve was determined from measuring two granulated CRMs of a type of polymer not found in our samples (low density polyethylene) and a BAM-H010 disc of ABS. Thus, neither of the curves considers the matrix effects, as the samples analysed are composed of a number of different polymers (i.e., ABS, HIPS, PS, PC + ABS, PMMA and PPE) [42].

Regression of Technique 1 by Technique 2

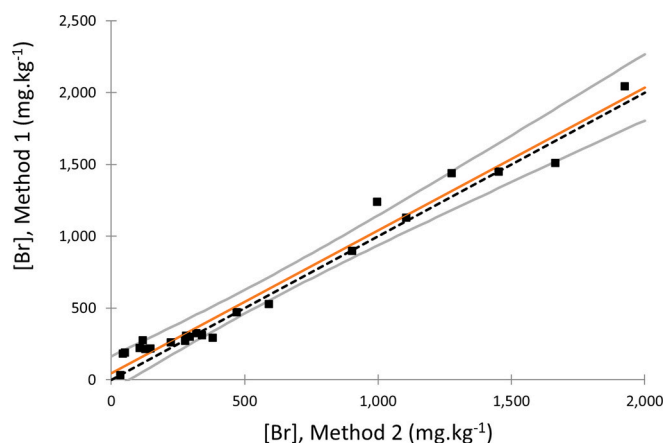


Fig. 11. Deming regression of Technique 1 by Technique 2.

Table 6
Bland & Altman test results.

Difference	-42.504
t (Observed value)	-2.217
t (Critical value)	2.074
DF	22
p-value (Two-tailed)	0.037
α	0.05

3.5. Identification of individual Brominated Flame Retardants

Results of BFR identification and quantification are presented in Table 7. In four samples (4,7,8 and 10) high Br concentrations were determined by h-XRF, however according to GC/MS results the Br does not come from any of the targeted compounds. This could mean that either: a) Br comes from a non-targeted brominated compound like TBP-DBPE, BEHTBP, BTBPE as it is known that for instance, in ABS, the use of BTBPE (1,2-bis(2,4,6-tribromophenoxy)ethane) as a substitute of traditional BFRs has been increasing [13]; or b) the recoveries for these samples were considerably low. However, we were not able to verify or reject either of the hypothesis as we did not analyse samples for further BFRs and recovery rates (the amount of each brominated compound extracted from the sample by the technique used for analysis) were not determined for each sample. Recoveries were determined for PBDEs in two certified reference materials made of LPDE (Polyethylene) and PP (Polypropylene), with rates between 72-154% and 75-150%, respectively. No recovery rates were determined for TBBPA or HBCDD.

3.6. Sb determination by ICP/OES

A statistical analysis of ICP/OES results shows there are three samples with %RSD (relative standard deviation) higher than 20% (see Table 8). No common factor was found to explain this deviation, so it is

assumed that it is associated with experimental aspects. These samples were not considered in further data analysis.

A linear correlation between Sb measured by h-XRF ($[Sb]_{XRF}$) and ICP/OES ($[Sb]_{ICP/OES}$) was established with a R^2 value of 0.993 (see Fig. 13). There is currently no certified reference material available for each of the polymers studied. Thus, it was not possible to determine extraction efficiencies and we were unable to do any further evaluation of the results as no relationships could be defined related to either the type of polymer or Sb concentration range.

4. Conclusions

We performed a thorough characterization of whole FPD plastic casings by on-site h-XRF analysis validated using reference materials and laboratory intercomparison. An assessment of the impact of analysis conditions related to dust setting on the samples showed that Br and Sb concentrations varied marginally when comparing before and after dust removal. Therefore, the presence of dust does not affect the validity of the h-XRF measurement for these parameters. As a good practice it is suggested that the area to be analysed is wiped with lint-free electrostatic cloth before the analysis.

An evaluation of the accuracy of measurements depending on the analysis time allowed the determination of 10 seconds counting time as optimal for h-XRF within the following concentration ranges: $LOD < [Br] < 3,500 \text{ mg kg}^{-1}$ and $LOD < [Sb] < 10,000 \text{ mg kg}^{-1}$, with a %Accuracy >95%.

Comparing the homogeneity of Br and Sb distribution within and between front and rear casings it was established that for the front casing the highest concentrations were more frequently found in the bottom left area, while for rear casings it was the centre area. However, considering the %Accuracy levels determined for $t_{analysis} = 10s$, we can conclude that in none of the cases would analysing only the centre or bottom left area on the rear and front casings respectively, have resulted

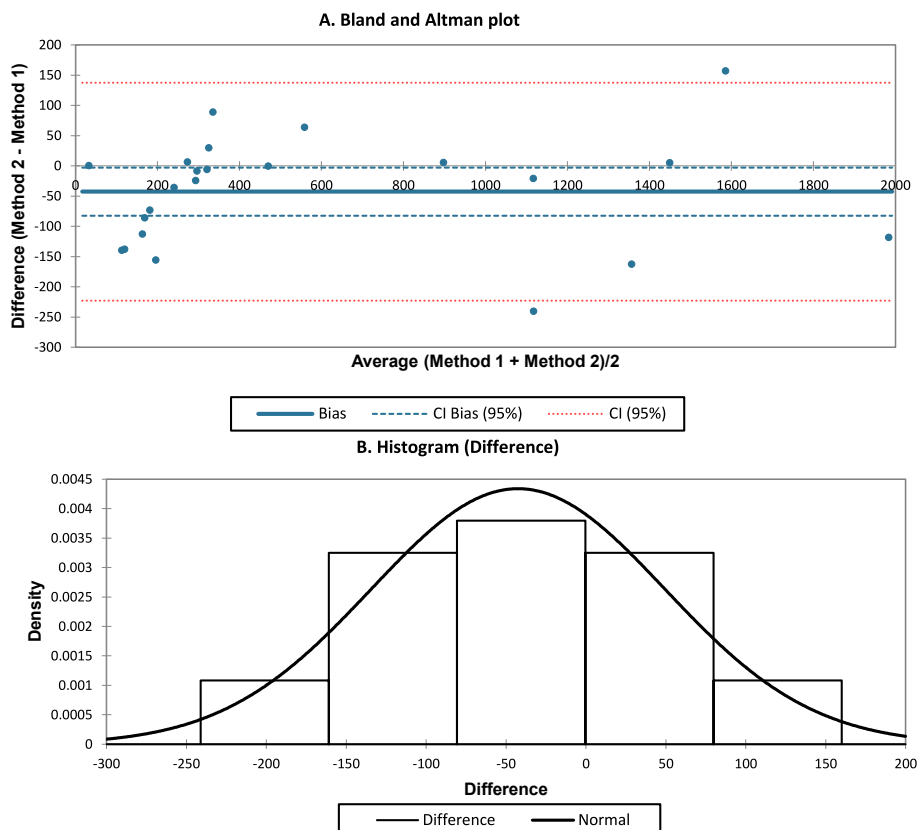


Fig. 12. Bland & Altman test results (A. B&A plot; B. Histogram of the differences between Technique 1 and Technique 2).

Table 7

BFR determination by GC/MS according to the method described in Drage et al., 2022 [31].

	Sample										
	1	2	3	4	5	6	7	8	9	10	
Polymer	ABS	HIPS	ABS	PS	PS	ABS	PS	HIPS	PC + ABS	HIPS	
Year of manufacture	2004	2006	2006	2007	2007	2007	2008	2011	2015	2016	
	Units (mg.kg ⁻¹)										
XRF	Br	189	3,159	7,782	113,377	485	133,296	66,120	85,072	192	154,897
	Sb	66	656	2,177	34,104	272	32,784	13,644	15,491	<LOD	24,915
GC/MS	BDE-28	<0.48	<0.48	<0.48	<0.48	<0.48	<0.48	<0.48	<0.48	<0.48	<0.48
	BDE-47	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
	BDE-99	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21	<0.21
	BDE-100	<0.24	056	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24	<0.24
	BDE-153	<0.24	9.59	0.26	<0.24	<0.24	0.29	0.40	<0.24	<0.24	<0.24
	BDE-154	<0.19	1.29	0.42	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19	<0.19
	BDE-183	23.15	95.11	22.59	22.70	22.65	24.03	198.87	22.86	23.11	16.79
	BDE-209	1.29	2,000	4.66	8.48	1.32	52,000	<0.71	4.47	3.94	1.19
	TBBPA	460	650	15,000	25.71	3.95	11.56	17.11	75.13	16.92	3.26
	a-HBCDD	<0.37	120.00	<0.37	0.46	<0.37	<0.37	1.22	1.59	<0.37	<0.37
	b-HBCDD	<0.42	22.52	<0.42	<0.42	<0.42	0.52	<0.42	<0.42	<0.42	<0.42
	g-HBCDD	1.14	23.13	0.44	1.86	0.73	2.55	1.49	1.34	0.37	0.43
	ΣPBDEs	24.45	2,100	27.92	31.18	23.97	52,000	20.27	27.33	27.05	17.97
	ΣHBCDD	1.14	170	0.44	2.33	0.73	3.08	2.71	2.93	0.37	0.43

Table 8

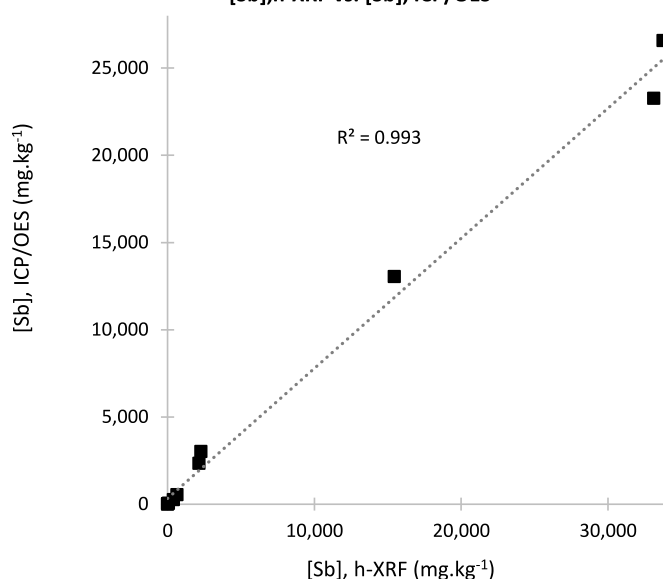
Sb concentrations determined by ICP/OES.

Sample	Polymer	Average [Sb] (mg.kg ⁻¹)	SD	%RSD
1	ABS	3,015	142.6	4.7
2	ABS	53	6.6	12.4
3	ABS	23,258	654.3	2.8
4	ABS	2,343	5.6	0.2
5	ABS	691	123.0	17.8
6	ABS	35	30.8	87.5
7	HIPS	13,043	172.1	1.3
8	HIPS	533	1.2	0.2
9	HIPS	256	47.8	18.7
10	HIPS	15,037	660.0	4.4
11	PC + ABS	0	0.0	0.0
12	PC + ABS	15	9.4	64.0
13	PC + ABS	22	0.4	1.7
14	PS	26,578	1094.2	4.1
15	PS	55	29.6	54.1

in a false negative (sorting and item a recyclable when it should have been sorted as POPs or POPs/HAZARDOUS). By further comparing results for both types of casings, we were able to determine that analysing the centre area of the rear casing is enough for sorting both samples with a %Accuracy level above 95%.

To validate our technique a ring trial exercise was conducted comprising 100 samples. Although the methods and equipment used were different, we obtained comparable and highly correlated results, demonstrating the suitability of the use of h-XRF for determining total Br in WEEE plastic samples in the LOD < [Br] < 2,000 mg kg⁻¹ concentration range. We provide evidence of a need to develop suitable certified reference materials that include the types of polymers found in this matrix as it would allow to have adequate calibration curves and correct results accordingly. We are aware of a plastic standard suitable for h-XRF analysis having been developed by Mans et al., 2007 [43], however, it is not commercially available.

As h-XRF measures total element concentrations and regulation establishes limit for specific compounds, we outsourced analysis for the determination of specific BFRs targeting those reported to be most commonly found in FPD plastics [9,24,29,31,33,44,45]. Ten samples were sent for GC/MS determination of PBDEs, TBBPA and HBCDD, and considering the results it is evident no definite conclusions can be drawn regarding a ratio between total Br and targeted BFRs concentrations. In

[Sb],h-XRF vs. [Sb], ICP/OES**Fig. 13.** Correlation between Sb concentrations determined by h-XRF and ICP/OES.

two of the samples, the compound exceeding the legal thresholds was BDE-209 (decaBDE), suggesting a conservative approach can be taken to consider all detected bromine is found as BDE-209 and that total Br concentration threshold could be set at 830 mg kg⁻¹. This is a reliable threshold that has been validated and is cost effective in terms of material segregation processes. There is low risk of false negatives and the risk of false positives is deemed acceptable in the industrial application of the technique. In addition, it has been widely reported [18,25,28,33,45–47] that the likelihood of h-XRF underestimating Br concentrations in plastic is virtually zero provided the measurement is performed under the proper conditions including the analyser window is rested directly on the surface of the sample, and the thickness of the sample is adequate (equal to or greater than the thickness defined as critical for that specific material).

Since 2015 there has been a downward trend in the levels of PBDEs

present in FPD plastics. While high concentrations of BFRs have been detected in these plastics ($>10,000$ mg kg⁻¹), currently only 10–20% correspond to PBDEs. However, PBDEs concentrations above 100,000 mg kg⁻¹ may still be found in articles manufactured before the restrictions on their use came into force [23]. This agrees with our result as regulated BFRs were found in samples manufactured prior to 2009, in line with banning of the use of certain PBDEs (i.e., tetra-BDE, penta-BDE, hexa-BDE and hepta-BDE) [25]. Considerably high Br concentrations were determined for later samples, however the low number of samples analysed and not having determined recovery rates does not allow us to make a definitive conclusion. This highlights the need to define regulatory limits based on elemental concentrations, e.g., total Br, which can be determined rapidly, easily, and inexpensively using h-XRF [21,27,28].

An Sb validation exercise showed that concentrations measured by h-XRF are consistently higher than those determined by ICP/OES. However, even though a strong linear correlation was determined between both methods, the lack of a certified reference material and absence of confirmed recovery rates, does not allow definitive values to be reported. Considering the concentration limit for Br at 830 mg kg⁻¹, and that according to published reports [18,25] and our own observations Sb is found in concentrations between 33 and 55% of Br, in no case will an item be classified as HAZARDOUS without having been classified as POPs, therefore there is no risk of false negatives concerning the presence of Sb.

The results of our study provide a comprehensive and highly detailed characterisation, demonstrating the reliability that can be achieved in categorizing hazardous/non-hazardous waste plastics from FPDs. This has implications for application by other waste management operators and policymakers in the more sustainable management of this waste stream. Furthermore, the defined methodology has great potential for the industry as it can be applied, with certain adaptations as needed, for the characterization of other WEEE plastics.

Author contributions

Cecilia Chaîne: Conceptualization, Methodology, Investigation, Data curation, Writing-original draft preparation, Writing-review and editing, Visualization. Andrew Hursthouse: Conceptualization, Resources, Writing-original draft preparation, Writing-review and editing, Visualization, Supervision, Project Administration, Funding acquisition. Aleksander Jandric: Investigation, Data curation, Writing-original draft preparation, Writing-review and editing. Bruce McLean: Resources, Writing-review and editing, Supervision, Project Administration, Funding acquisition. Brian McMahon, Jim McNulty: Resources, Supervision, Project Administration, Funding acquisition. Jan Miller, Iain McLellan, Evi Viza: Resources, Supervision, Project Administration, Funding acquisition. Stefan Salhofer: Resources, Supervision.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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