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Turner, Andrew

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# **Field-portable-XRF reveals the ubiquity of antimony in plastic consumer products**

Andrew Turner\*

School of Geography, Earth and Environmental Sciences, Plymouth University, Drake  
Circus, Plymouth PL4 8AA, UK

[\\*aturner@plymouth.ac.uk](mailto:*aturner@plymouth.ac.uk)

Montserrat Filella

Institute F.-A. Forel, University of Geneva, Boulevard Carl-Vogt 66, CH-1205 Geneva,  
Switzerland

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31 **Abstract**

32 Very little systematic information exists on the occurrence and concentrations of  
33 antimony (Sb) in consumer products. In this study, a Niton XL3t field portable-x-ray  
34 fluorescence (FP-XRF) spectrometer was deployed in situ and in the laboratory to  
35 provide quantitative information on Sb dissipated in plastic items and fixtures  
36 (including rubber, textile and foamed materials) from the domestic, school, vehicular  
37 and office settings. The metalloid was detected in 18% of over 750 products analysed,  
38 with concentrations ranging from about 60 to 60,000  $\mu\text{g g}^{-1}$ . The highest  
39 concentrations were encountered in white, electronic casings and in association with  
40 similar concentrations of Br, **consistent with the use of antimony oxides (e.g.  $\text{Sb}_2\text{O}_3$ )**  
41 **as synergistic flame retardants**. Concentrations above 1000  $\mu\text{g g}^{-1}$ , and with or without  
42 Br, were also encountered in paints, piping and hosing, adhesives, whiteboards,  
43 Christmas decorations, Lego blocks, document carriers, garden furniture, upholstered  
44 products and interior panels of private motor vehicles. Lower concentrations of Sb  
45 were encountered in a wide variety of items but its presence (without Br) in food tray  
46 packaging, single-use drinks bottles, straws and small toys were of greatest concern  
47 from a human health perspective. These observations are consistent with **the use of**  
48 **antimony compounds as catalysts** in the production of polyethylene terephthalate but  
49 also suggest that electronic casings are widely recycled for the manufacture of a  
50 variety of consumer products. Further research is required into the mobility of Sb  
51 when dissipated in new, recycled and aged polymeric materials.

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53

54 **Keywords:** FP-XRF; antimony; household; plastics; bromine; recycling

## 55 **1. Introduction**

56 One of the main features of the current use of chemical elements is their application in  
57 materials at small concentrations by weight but in a large variety of products. This  
58 results in ubiquity in the environment but strongly hinders the ready and routine  
59 determination of their presence. Measuring and monitoring trace elements in final  
60 products is necessary for different reasons, ranging from assessing their potential  
61 toxicological and ecotoxicological effects to an evaluation of in-use stocks for life-  
62 cycle assessments.

63

64 In this context, antimony (Sb) is a particularly interesting element for two reasons.

65 Firstly, its use increased significantly in the first decade of the present century (total  
66 antimony consumption grew by about 40% and from 147,000 to 206,000 tonnes  
67 between 2000 and 2011; USGS, 2016) and, although global production has receded  
68 slightly since 2011, it is predicted to increase from 2015 to 2020 (Dupont et al., 2016).

69 Secondly, the type of use of Sb has shifted from applications where it can be  
70 recovered (e.g., as an additive in lead alloys) to those where recycling is not possible  
71 because of its dissipation in the product (e.g., as a catalyst in polyethylene  
72 terephthalate (PET) manufacturing and as a synergistic flame retardant)  
73 (Zimmermann and Gößling-Reisemann, 2013; Talens Peiró et al., 2013; Ciacci et al.,  
74 2015). At present, Sb use as a catalyst and flame retardant accounts for about 60% of  
75 its total production while applications in metallurgy account for about 35% (Schwarz-  
76 Schampera, 2014).

77

78 Despite the cumulative toxicity of Sb and its similarity with As in many biological  
79 respects, the element was rather poorly studied until the mid-1990's. Specifically, a

80 possible link between sudden infant death syndrome (SIDS) and volatile antimony  
81 hydride generated via the biomethylation of antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) used as a  
82 flame retardant in cot mattress covers triggered a strong interest in the metalloid  
83 (Richardson, 1990, 1994). More recently, scientific and media attention has been  
84 diverted to the presence of measurable concentrations of antimony in bottled water  
85 (Shotyk et al., 2006; Westerhoff et al., 2008), fruit juices (Hansen et al., 2006) and  
86 ready-meals (Haldimann et al., 2013) arising from the leaching of Sb from PET  
87 containers. PET is a highly favourable and widely used material for food and drink  
88 packaging and oven-proof and reheatable meals because of its thermal and physical  
89 stability, low density and recyclability (Chapa-Martinez et al., 2016).

90

91 Given the properties and applications of Sb, there are reasons to suspect that the  
92 presence of the element in our daily lives may be more widespread than is implied  
93 from current or past research. However, outside of the grey literature, systematic,  
94 quantitative information on the occurrence of Sb in the domestic and consumer setting  
95 appears to be limited to a few measurements performed on PET bottles (Chapa-  
96 Martinez et al., 2016) and other food-contact polymers (Puype et al., 2015), toys  
97 (Korfali et al., 2013) and end-of-life televisions (Saphores and Milovantseva, 2011).  
98 To this end, we describe the use of field-portable-x-ray fluorescence (FP-XRF)  
99 spectrometry to determine the presence, distribution and concentrations of Sb in  
100 products from the indoor environment. The focus is on synthetic, polymeric materials  
101 (plastics), where the element is most likely to be present as a catalyst or added as a  
102 flame retardant, that are encountered in the household, office, school and vehicular  
103 environments. Simultaneous measurements of Br and Cl are also performed in order

104 to determine the type of materials and flame retardants that Sb is associated with in  
105 different products.

106

## 107 **2. Materials and methods**

### 108 *2.1. Material access, collection and categorisation*

109 Antimony considered in the present study was bound to moulded plastics, rubbers,  
110 textiles, foams, fibres and waxes, or incorporated into paints and coatings applied to  
111 various products, structures and surfaces. A total of 750 items and fixtures (‘samples’)  
112 were accessed or sourced from a variety of domestic dwellings in Plymouth, three  
113 private vehicles registered between 2004 and 2016, offices around the Plymouth  
114 University campus, a local primary school and nursery, and a hardware chain store.

115

116 Depending on their location and principal use, samples were categorised according to  
117 the list given in Table 1. However, it must be appreciated that several of the categories  
118 are not mutually exclusive (for example, electronic toys, constructed versus  
119 upholstered flooring, storage for food and for sports equipment) and that some  
120 samples comprised distinct components that were analysed and categorised  
121 separately. While the surface or coating of most samples was targeted, occasional  
122 end-of-life electronic products were dismantled and interior components analysed  
123 individually.

124

### 125 *2.2. XRF analysis*

126 Samples were analysed energy-dispersive FP-XRF using a Niton XL3t 950 He  
127 GOLDD+ that was employed handheld and in situ or configured in the laboratory in  
128 an accessory-stand. The Niton XL3t employs a miniature x-ray tube with a silver

129 transmission anode that operates at up to 50 kV of high voltage and 200  $\mu$ A of current  
130 as the source of sample excitation, and is fitted with a geometrically optimised large  
131 area silicon drift detector to detect fluorescent x-rays from the sample. The  
132 concentrations of Sb, based on characteristic peaks at 26.359 KeV ( $K\alpha$ ) and 3.604  
133 KeV ( $L\alpha$ ) (Figure 1), were determined in a ‘plastics’ mode through a standardless,  
134 fundamental parameters-based alpha coefficient correction model. This iterative  
135 approach accounts for background matrix effects by describing characteristic x-ray  
136 intensities using mathematical equations that tie together the physics of the interaction  
137 of x-rays with sample components, and has a wide dynamic range that is independent  
138 of the size and shape of the surface (Bosco, 2013). Concentrations of Br and Cl were  
139 also recorded during sample analyses, as indicators of the presence of halogenated  
140 flame retardants and polymer chlorination (and polyvinyl chloride, PVC).

141

142 Because plastics are composed of light elements that are weak absorbers and  
143 relatively strong scatterers of x-rays, below a critical thickness the measured intensity  
144 of characteristic x-rays will be dependent on both the analyte concentration and the  
145 depth of the sample. For polyethylene, for example, the critical thickness is about 9  
146 mm while for PVC the presence of chlorine results in a corresponding thickness of  
147 around 5 mm; for polymers containing heavier elements, including Sb and Br, critical  
148 thickness depth is reduced compared with that of the pure material. In the plastics  
149 mode, the Niton XL3t incorporates a thickness correction algorithm down to 50  $\mu$ m  
150 that employs a compensation for mass absorption based on Compton scatter so that  
151 variations in density are factored in. **Although the corrective algorithm is embedded in**  
152 **the fundamental parameters code and inaccessible to the user, it has been empirically**

153 defined for various elements (including Sb, Br and Cl) in a variety of plastics  
154 elsewhere (Turner and Solman, 2016).

155

156 In the present study, sample thickness was determined through the flattest or  
157 smoothest ('measurement') surface using 300 mm Allendale digital callipers, and to  
158 increase the effective depth and flatness of thin or hollow samples analysed in the  
159 accessory stand, items were cut (with scissors, pliers or a blade), folded or layered.  
160 The corrective algorithm was employed for all samples whose measured thickness  
161 was less than 30 mm, while an estimated value was applied to all objects and  
162 components whose interiors were inaccessible or that were fixed to or components of  
163 walls, floors, windows, doors and appliances. A thickness of 0.05 mm was assumed  
164 when analysing painted surfaces or paints and cosmetics that had been applied to and  
165 oven-dried on glass slides.

166

167 In the laboratory, the XRF was used in a collapsible bench-top accessory stand  
168 (Thermo Scientific SmartStand, with internal dimensions of 20 cm x 20 cm x 10 cm;  
169 PN 420-017) and was connected to a laptop computer via USB and a remote trigger.  
170 Samples were placed on the stainless steel base plate of the accessory stand above the  
171 detector window or, for samples smaller than the 8 mm window diameter, on to a  
172 SpectraCertified Mylar polyester 3.6  $\mu\text{m}$  film that was carefully positioned centrally  
173 above the window. On closing the shield of the stand, measurements with appropriate  
174 thickness correction and collimation (3 mm or 8 mm beam width) were activated  
175 through the laptop. Specifically, an initial, ~ 2-second matrix evaluation based on the  
176 measurement of characteristic chlorine peaks (and defining PVC as Cl > 15% by  
177 weight) was succeeded by an analysis time of between 60 and 200 seconds,

178 comprising counting periods equally distributed between a low energy range (20 kV  
179 and 100  $\mu\text{A}$ ) and main energy range (50 kV and 40  $\mu\text{A}$ ). Spectra were quantified by  
180 fundamental parameter coefficients to yield elemental concentrations on a dry weight  
181 basis (in  $\mu\text{g g}^{-1}$ ) and with a counting error of  $2\sigma$  (95% confidence). Polyethylene  
182 reference discs supplied by the manufacturer and certified for Sb (PN 180-619,  
183 LOT#T-18) and Br (PN 180-554, batch SN PE-071-N) were analysed at the beginning  
184 and end of each 1-4 h sample measurement session, and spectra and elemental  
185 concentrations arising from each session were subsequently downloaded to the laptop  
186 using Niton data transfer (NDT) PC software.

187

188 For in situ measurements of permanent fixtures and objects too large to be contained  
189 by the laboratory accessory stand, the XRF was used handheld and in situ. Here, the  
190 nose was pressed firmly against the measurement surface, ensuring that the detector  
191 window was completely covered and that there was sufficient shielding and/or  
192 distance behind. The instrument was activated by the operator using the trigger  
193 mechanism and the touch-screen control panel, and where possible a Thermo  
194 Scientific backscatter collar shield was clipped on to the nose of the instrument. The  
195 shield consists of tungsten-impregnated PVC that extends and tapers outwardly from  
196 the propagation axis to a radius of about 10 cm and, while designed to lie proximate to  
197 the material being inspected, has some degree of flexibility to conform to the contours  
198 of irregularly-shaped surfaces. As above, reference discs were analysed at the  
199 beginning and end of each measurement session while placed on a solid surface and  
200 data were subsequently downloaded to the laptop via the NDT software.

201

202 *2.3. Sample digestion and analysis by ICP*

203 In order to validate the XRF approach, an independent measure of the Sb content of  
204 synthetic, polymeric materials was performed by inductively coupled plasma-optical  
205 emission spectroscopy (ICP-OES) following digestion in Fisher Scientific TraceMetal  
206 grade acids. Specifically, 50 to 100 mg offcuts or slices of 14 samples of varying  
207 characteristics (in terms of colour, use-origin, thickness, density and Sb content as  
208 returned by the FP-XRF) were prepared with a stainless steel blade and a pair of pliers  
209 before being accurately weighed into individual 100 ml borosilicate Tecator tubes.  
210 Three ml of concentrated sulphuric acid was added to each tube and the contents  
211 heated to 300°C for 2 h in an aluminium digestion block before concentrated HNO<sub>3</sub>  
212 was added dropwise until solutions became pale yellow or colourless. Digests were  
213 then allowed to cool overnight before being transferred to 50 ml glass volumetric  
214 flasks and diluted with 2% HNO<sub>3</sub>. **To any digests containing a visible precipitate,**  
215 **concentrated ammonia solution was added dropwise until the solids cleared.**  
216 Procedural controls were undertaken in triplicate likewise but in the absence of solid  
217 material.

218

219 Digests were analysed for Sb at a peak emission wavelength of 206.833 nm by ICP-  
220 OES using a Thermo Scientific iCAP 7400. The instrument was calibrated using four  
221 standards and a blank prepared by serial dilution of a CPI International standard in 2%  
222 HNO<sub>3</sub>, with settings as follows: exposure time = 2 s; RF power = 1150 W; nebuliser,  
223 coolant and auxiliary gas flows = 0.50, 12 and 0.5 L min<sup>-1</sup>, respectively; viewing  
224 height = 12 mm; uptake time = 50 s; wash time = 15 s.

225

## 226 **3. Results**

### 227 *3.1. Detection limits*

228 The limits of detection (LODs) of FP-XRF spectrometers are dependent on the  
229 response of specific elements to primary x-rays and the energies of their characteristic  
230 x-rays, detector resolution, mode of application (or current, peak voltage and beam  
231 filtration), counting time, sample thickness, and physical and chemical characteristics  
232 of the material. The Niton XLT3t series of analysers define LODs from counting  
233 errors as three standard deviations ( $1.5 \times 2\sigma$ , or 99.7% confidence interval), and  
234 concentrations are delivered in the NDT output only where they exceed this threshold  
235 with calculated detection limits returned otherwise. LODs stated by the manufacturer  
236 for Sb in pure polyethylene and in PVC (both of unspecified thickness) and for a 30-  
237 second total counting time configured in plastics mode are  $22 \mu\text{g g}^{-1}$  and  $25 \mu\text{g g}^{-1}$ ,  
238 respectively; the respective LODs for Br are  $3 \mu\text{g g}^{-1}$  and  $8 \mu\text{g g}^{-1}$ , and for Cl in  
239 polyethylene the LOD is  $40 \mu\text{g g}^{-1}$ .

240

241 Under the operating conditions of the instrument described above, LODs for Sb were  
242 highly variable, reflecting the diverse and complex nature of the samples. Respective  
243 minimum and maximum LODs were about  $19 \mu\text{g g}^{-1}$  and  $400 \mu\text{g g}^{-1}$ , with increasing  
244 values generally related to decreasing thickness and counting time. By comparison,  
245 LODs for Br and Cl ranged from about  $3 \mu\text{g g}^{-1}$  to  $50 \mu\text{g g}^{-1}$  and about  $45 \mu\text{g g}^{-1}$  to  $200$   
246  $\mu\text{g g}^{-1}$ , respectively.

247

### 248 *3.2. Accuracy and precision*

249 Table 2 shows the results of multiple analyses of the two reference discs  
250 manufactured by Niton. Regarding the disc impregnated with Sb, concentrations  
251 measured by the XRF both in the accessory stand and handheld are close to the  
252 certified concentration, with marginally better accuracy and precision achieved when

253 the instrument was employed in the stand. With respect to the disc impregnated with  
254 Br, mean measured concentrations are within the 95% confidence interval of certified  
255 values, with a marginally lower accuracy but greater precision achieved in the stand.  
256 Multiple analyses of various samples revealed precisions for Sb and Br that improved  
257 with absolute concentration and thickness but that were always better than 20% (as  
258 relative standard deviation) in both types of instrument application.

259

260 A comparison of the concentrations of Sb in various samples of plastic, paint and  
261 foam returned by FP-XRF and by ICP-OES following acid digestion is shown in  
262 Figure 2. (Note that in the six cases where Sb was not detected by the XRF, ICP  
263 measurements did not exceed the corresponding LOD of the XRF.) The best fit line  
264 forced through the origin reveals a gradient of 1.3, indicating that, on average, the  
265 XRF returns a concentration of Sb that is about 30% higher than that delivered by the  
266 ICP. The discrepancy may be attributed to spatial heterogeneity of Sb within samples  
267 (XRF will determine elemental concentrations at a specific location while ICP relies  
268 on digestion and analysis of whole sections), incomplete acid digestion or partial loss  
269 of volatile Sb compounds in some samples, and, with respect to XRF, inaccuracies in  
270 thickness estimation and spectral interferences arising from material below or within  
271 the target surface. Regardless of the causes of such a discrepancy, however, the  
272 statistically significant proportionality between Sb concentrations returned by the FP-  
273 XRF and those delivered by an independent method, coupled with a correlation  
274 coefficient exceeding 0.9, meet the definitive level criterion according to US EPA  
275 validation guidelines (Environmental Protection Agency, 2007).

276

277 *3.3. Occurrence and distribution of Sb*

278 Table 3 provides a summary of the number of XRF analyses performed in each  
279 sample category. Also shown is the number of cases in which Sb was detected, along  
280 with the number of cases in which Sb was encountered in PVC or co-associated with  
281 either Br or (non-PVC-based) Cl or with both Br and Cl. Overall, Sb was detected in  
282 150 cases, or in about 18% of all analyses, and relative abundance was greatest in  
283 vehicle interiors (37%) and lowest in the cleaning-storage category (8%). Its  
284 occurrence in PVC was greatest in vehicle interiors and in electronic casings or  
285 components, with no Sb detected in PVC products in the food-drink, toys-hobbies or  
286 office-stationery categories. Association with Br was most frequent on both a number  
287 and percentage basis in the electronics category while no co-existence was detected in  
288 the food-drink category. Association of Sb with Cl occurred in fewer cases overall but  
289 across all sample categories, while association with both Br and Cl was observed in  
290 only 17 samples among six categories.

291

292 The distribution and summary statistics for Sb concentrations among the different  
293 categories are shown in Table 4, while figure 3 illustrates some of the specific  
294 products in which the XRF returned concentrations of the metalloid. Electronic  
295 samples exhibited the highest mean and median concentrations and a concentration  
296 range that spanned nearly three orders of magnitude. The highest individual  
297 concentrations of about  $50,000 \mu\text{g g}^{-1}$  were encountered in a variety of white products,  
298 including a multi-plug adaptor, telephone-modem connector, fan heater, central  
299 heating thermostat and a number of collars around connectors of long-life light bulbs.  
300 All of these items were associated with concentrations of Br that were in excess of but  
301 less than double the respective concentrations of Sb, but none of the items was PVC-  
302 based and only one contained detectable Cl. Other products containing Sb at

303 concentrations in excess of 10,000  $\mu\text{g g}^{-1}$  included a number of plugs and television  
304 casings, a printed circuit board, several PVC wire insulators and a USB-connector  
305 cover. These products did not always contain measurable Br and were a variety of  
306 colours, but principally black or white. Items that contained concentrations of Br in  
307 excess of 10,000  $\mu\text{g g}^{-1}$  but no measurable Sb included a games consol, several  
308 printed circuit boards, remote controls and extension leads, and components of  
309 various computer mouses.

310

311 In the food-drink category, measurable concentrations of Sb, ranging from about 200  
312 to 900  $\mu\text{g g}^{-1}$ , were encountered in packaging trays for vegetables, confectionary, fish  
313 and ready meals, and in straws, single-use drink bottles and a cool bag. While Br was  
314 not detected in these products, Cl often occurred at concentrations lower than  
315 corresponding levels of Sb.

316

317 With a mean Sb concentration of about 1600  $\mu\text{g g}^{-1}$  and a concentration range  
318 spanning two orders of magnitude, Sb was detected in a wide variety of products from  
319 the clothing-upholstery category. The highest concentrations (of several thousand  $\mu\text{g}$   
320  $\text{g}^{-1}$ ) were **encountered in** combination with similar or higher corresponding  
321 concentrations of both Br and Cl in a futon cover and in cushioning from a garden  
322 chair and dressing table stool. Items of clothing in which Sb was detected at several  
323 hundred  $\mu\text{g g}^{-1}$  included a safety jacket, raincoats, sports shirts and items of fancy  
324 dress, most of which contained similar concentrations of either Br or Cl and one of  
325 which was PVC-based.

326

327 Antimony was detected in three products classified as cleaning-storage and with a  
328 mean concentration of  $355 \mu\text{g g}^{-1}$ ; specifically, a watering can, a PVC door-stop and,  
329 in association with both Br and Cl, a luggage tag. In the construction-plumbing  
330 category, mean, minimum and maximum concentrations of Sb were about 1600, 100  
331 and  $13,000 \mu\text{g g}^{-1}$ , respectively. The majority of cases and the highest concentrations  
332 were associated with plumbing (PVC-hosing, radiator caps, piping and pipe  
333 insulation), although Sb was also detected in wall and door paints, PVC-flooring and a  
334 window frame. In most products in this category, either Br or Cl was also detected at  
335 concentrations similar to corresponding Sb concentrations. With respect to toys-  
336 hobbies, Sb was detected with a mean and range of concentrations similar to  
337 respective values for the construction-plumbing category, with concentrations of  
338 several thousand  $\mu\text{g g}^{-1}$  encountered in Christmas beads, artists' paints and  
339 contemporary Lego bricks. Co-association with similar concentrations of Br was  
340 found in various Christmas decorations and a toy car and with variable levels of Cl in  
341 a variety of products that included 35 mm negative slides, soft toys, game counters  
342 and the plastic sleepers of an electric railway track.

343

344 The office-stationery and leisure-sport categories exhibited similar occurrences and  
345 concentration distributions of Sb, with mean values of around  $800 \mu\text{g g}^{-1}$  and ranges  
346 from about 100 to  $2500 \mu\text{g g}^{-1}$ . Among items with the highest concentrations recorded  
347 were a foot pump, the seating of an exercise bike and the plastic top of a trophy, all of  
348 which contained Br at concentrations exceeding those of Sb, and, in the absence of Br  
349 (and Cl), PVC adhesive taping, two whiteboards and a document carrier.

350

351 Regarding vehicle interiors, the mean concentration of Sb was about 1700  $\mu\text{g g}^{-1}$ , with  
352 a concentration range that spanned two orders of magnitude. Concentrations greater  
353 than 1000  $\mu\text{g g}^{-1}$  were measured in panels, armrests and seats that were non-PVC-  
354 based, but Br and Cl were only detected in two cases each (and at concentrations  
355 exceeding the corresponding Sb concentrations). Where Br was detected in the  
356 absence of measurable Sb, however, concentrations were always less than 10  $\mu\text{g g}^{-1}$ .

357

#### 358 **4. Discussion**

359 This study has revealed the presence of Sb in a wide range of polymeric products and  
360 components from the indoor environment. The highest concentrations, and exceeding  
361 1% by weight, are largely restricted to electronic casings, and an association with Br  
362 or Cl is consistent with use of Sb as a synergistic, free radical-quenching flame  
363 retardant in the presence of halogenated compounds (including PVC, which itself  
364 exhibits inherent flame retardant properties). The majority of the highest  
365 concentrations of Sb in non-electronic samples were encountered in upholstered  
366 products or fixtures in the home and vehicular environments, and, as above, their  
367 association with Br or Cl is consistent with the use of Sb as a flame retardant synergist  
368 in soft furnishings.

369

370 Where Sb occurs at concentrations below 1000  $\mu\text{g g}^{-1}$  and without Br or Cl, the  
371 metalloid is most likely present as catalytic residue from the manufacture of PET  
372 (typical concentrations of Sb in the polyester are a few hundred  $\mu\text{g g}^{-1}$ ; Bach et al.,  
373 2012). Most single-use food and drink items containing Sb were labelled as PET, and  
374 we suspect that this polymer has widespread use across all sample categories  
375 considered. Where Sb is encountered at concentrations of several thousand  $\mu\text{g g}^{-1}$  (i.e.

376 exceeding levels in PET products) and in the absence of Br or Cl, it is possible that  
377 the metalloid is used as a pigment for plastics and paints. For example, the occurrence  
378 of Sb in white wall paints and whiteboards is consistent with the use of  $\text{Sb}_2\text{O}_3$  as a  
379 moderately opaque white pigment (Abel, 2000), while its occurrence in red products  
380 may reflect the use of one or more antimony sulphide compounds (Eastaugh et al.,  
381 2008).

382

383 In a diversity of samples, including game mats, soft toys, rucksacks, ink cartridges,  
384 football shirts, safety jackets, insulating foam, currency and picture frames,  
385 concentrations of Sb of a few hundred  $\mu\text{g g}^{-1}$  occurred in combination with similar  
386 concentrations of Br or Cl. A recent study by Puype et al. (2015) has also reported  
387 comparable concentrations of both Sb and Br in a number of black, polymeric food-  
388 contact articles purchased on the European market. Since concentrations of both  
389 elements are too low to offer adequate flame retardancy, it would appear that many  
390 polymeric household items that have no reason to be fire-resistant are constructed, at  
391 least in part, from end-of-life electronic products.

392

393 Critical to the human health risks posed by Sb encountered in polymeric materials are  
394 the extents of mobilisation of the metalloid from the matrix. Regarding non-  
395 occupational dermal exposure, so little is known that the National Research Council  
396 (2000) assumed that ionised antimony trioxide permeates the skin at the same rate as  
397 water, ( $10^{-3} \text{ cm h}^{-1}$ ). A maximum dermal exposure level of  $20 \mu\text{g kg}^{-1} \text{ d}^{-1}$  was then  
398 derived for an individual spending 25% of their time on Sb-treated upholstered  
399 furniture. Of more general significance for human Sb exposure, however, is the  
400 leachability of the metalloid from both food contact products and toys. In water and

401 juices bottled in PET containers, leaching of Sb has been shown to be a function of  
402 time, temperature, pH and insolation. Resulting aqueous concentrations are typically  
403 well below admissible levels for the European Union ( $5 \mu\text{g L}^{-1}$ ) and the US EPA ( $6$   
404  $\mu\text{g L}^{-1}$ ) (Hansen and Pergantis, 2006; Shotyk et al., 2006; Greifenstein et al., 2013;  
405 Chapa-Martinez et al., 2016) but are closer to a  $1 \mu\text{g L}^{-1}$  limit recently updated as a  
406 Public Health Goal (PHG) for Californian drinking water (Qiao, 2016). Mobilisation  
407 of Sb into pre-packaged food from PET trays heated by microwave and oven has also  
408 been documented, with quantities of the metalloid in cooked meals of up to about 35  
409  $\mu\text{g}$  (Haldimann et al., 2007). Although higher than quantities of Sb in many litres of  
410 bottled water, consumption of several of the most contaminated ready meals by an  
411 individual would still be below tolerable daily intake limits for the element ( $360 \mu\text{g}$   
412 for an adult of 60 kg) (WHO, 2003).

413

414 Antimony is one of eight elements for which migratable limits, based on extractability  
415 in dilute HCl (pH 1.8) at  $37^\circ\text{C}$  for two hours, exist in toys and other objects mouthable  
416 by young children (e.g. pens and crayons). The original European toy safety standard  
417 on the migration of certain elements (EN71-3: 1994 or BS EN71-3: 1995; British  
418 Standards Institution, 2006) defined a limit for Sb of  $60 \mu\text{g g}^{-1}$ , a value that was  
419 subsequently adopted as a maximum soluble concentration by the US Consumer  
420 Product Safety Commission (Cobb, 2015). Under this classification, products  
421 analysed by XRF and returning a concentration of Sb exceeding the threshold would  
422 require subsequent extraction in HCl in order to evaluate migratability. More recently,  
423 however, a revised version of the European standard (EN71-3: 2009) outlines  
424 migratable limits that are dependent on the characteristics of the material. Thus,  $45 \mu\text{g}$   
425  $\text{g}^{-1}$  is adopted for brittle or pliable items,  $11.3 \mu\text{g g}^{-1}$  for liquid or sticky products and

426 560  $\mu\text{g g}^{-1}$  for scraped off materials, including paints and plastics (European  
427 Parliament and the Council of the European Union, 2009). In the present study, all  
428 samples in the toys-hobbies categories in which Sb was detected by XRF ( $n = 24$ )  
429 were in the latter European material classification, with concentrations exceeding 60  
430  $\mu\text{g g}^{-1}$  in all cases and exceeding 560  $\mu\text{g g}^{-1}$  in 13 samples. Although the migratability  
431 of Sb was not determined in these samples, Ciu et al. (2015) provide a mean HCl-  
432 extraction of Sb from various newly purchased toys and jewellery of 13.4%. Applying  
433 this figure to the current results, two samples (red and gold Christmas beads) would  
434 exceed the current European limit for migratable Sb in plastic products.

435

436 From an environmental perspective, Sb is a concern because of its potential  
437 mobilisation from polymeric waste items that are disposed of by landfill or  
438 incineration or that are dismantled-recycled. Although regulations exist in Europe  
439 limiting air-stack emissions of Sb (2000/76/EC; European Parliament and the Council  
440 of the European Union, 2000) and concentrations of leachable Sb in inert waste  
441 acceptable as landfill (Council of the European Union, 2003a), there does not appear  
442 to be an unawareness of the ubiquity of Sb in everyday items that the present study  
443 has highlighted. The high proportion of Sb in current use as a flame retardant  
444 synergist in electronic products and components should ensure that a significant  
445 fraction of waste containing **Sb is reused**, recycled or recovered in accordance with  
446 the requirements of the European Waste Electrical and Electronic Equipment (WEEE)  
447 Directive (2002/96/EC; European Parliament and the Council of the European Union,  
448 2003). However, unlike many other heavy metals and flame retardants, Sb was not  
449 included in the original Restriction of Hazardous Substances (RoHS) Directive  
450 (2002/95/EC; Council of the European Union, 2003b) that limits use in electrical and

451 electronic equipment. Moreover, according to a subsequent investigation into  
452 substances not regulated by the RoHS Directive, it was concluded that, despite  
453 concerns about potential impacts on the marine environment and on sediment from  
454 flame-retardant back-coated products, the limited data available on Sb precluded  
455 justification for its inclusion (Groß et al., 2008). A consequence of this is that when  
456 electronic plastic waste is recycled, there is no consideration of the subsequent use  
457 and fate of Sb dissipated within the polymeric matrix.

458

## 459 **5. Conclusions**

460 FP-XRF has revealed that Sb is encountered in a wide range of polymeric consumer  
461 products in the household, school, vehicular and office settings, principally as either a  
462 catalyst in the production of PET or a synergistic flame retardant with halogenated  
463 compounds. In association with Br, concentrations are highest and a few percent on a  
464 weight basis in plastic electronic casings, but from a health perspective, the presence  
465 of lower quantities of catalytic Sb in food packaging and small toys is of greatest  
466 concern. Aside from these sources, it appears that an increasing, indirect source of the  
467 metalloid is related to the recycling of electronic plastic casings and housings. Further  
468 research into the toxicity of Sb and its mobility when dissipated in the polymeric  
469 matrix is required, while reconsideration of the means of disposal and recycling of Sb-  
470 rich electronic plastic waste is called for.

471

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Table 1: Categorisation of the items and fixtures considered in the present study.

electronics	food-drink	clothing-upholstery	cleaning-storage	construction-plumbing	toys-hobbies	office-stationery	leisure-sport	vehicle interiors
fridges, freezers laptops, keyboards radios televisions, screens cables alarms plugs, adaptors phones cameras chargers hairdryers, irons light switches light bulbs headphones	packaging utensils plates mugs bottles ice packs straws lunch boxes tablet strips coffee pods	clothing sofas, cushions carpets, rugs shoes, boots rucksacks handbags wallets table cloths mattresses, pillows curtains	cans, canisters drawers bottles, tubes, lids polystyrene bags, sacks buckets boxes cartridges tools pegs paints brushes suitcases coathangers	doors, windows vinyl flooring drainage pipes hosing insulating foam baths and showers coving construction board worktops panels painted walls	figures cars, trains games, puzzles bath toys book covers fake jewellery building blocks musical instruments book covers pens, paints, crayons marbles, counters	pens adhesives document cases office equipment marker boards printing equipment lanyards stands, trays packaging	exercise bikes balls racquets, bats garden furniture cycle helmets tape trophies sports bags bike accessories bodyboards cosmetics sunglasses currency, cards CDs, DVDs	dashboards panels radios steering wheels seats, belts armrests flooring visors roof upholstery footplates chargers toll tags mats

Table 2: A comparison of reference and measured concentrations ( $\mu\text{g g}^{-1}$ ) of Sb and Br in polyethylene discs of 31 mm diameter and 13 mm depth supplied by Niton. Note that reference concentrations are given with estimates of errors at the 95% confidence level arising from an unspecified number of analyses while measured concentrations are shown as the mean with one standard deviation ( $n = 20$ ).

Reference disc	reference concentration	measured concentration in stand	measured concentration handheld
Sb (PN 180-619)	$94 \pm 10$	$93 \pm 11$	$91 \pm 16$
Br (PN 180-554)	$495 \pm 20$	$500 \pm 30$	$511 \pm 19$

Table 3: Number of analyses performed on samples from each category, and the number of cases in which PVC, Sb, Br and (non-PVC) Cl were detected together with the number of cases in which Sb was detected in PVC, and with Br or Cl and with Br and Cl.

	analyses	PVC	Sb	Br	Cl	Sb-PVC	Sb-Br	Sb-Cl	Sb-Br-Cl
electronics	194	16	47	75	59	8	32	10	5
food-drink	108	2	14	6	36	0	0	7	0
clothing-upholstery	76	10	14	18	28	1	8	8	4
cleaning-storage	44	3	3	2	12	1	1	3	1
construction-plumbing	56	15	14	11	8	2	6	4	0
toys-hobbies	162	12	24	14	74	0	7	16	4
office-stationery	55	7	9	9	14	0	2	2	1
leisure-sport	85	13	11	13	22	1	6	3	2
vehicle interiors	38	5	14	9	13	3	4	2	0
<b>total</b>	<b>818</b>	<b>83</b>	<b>150</b>	<b>157</b>	<b>266</b>	<b>16</b>	<b>66</b>	<b>55</b>	<b>17</b>

Table 4: Summary statistics and distributions of Sb concentrations (in  $\mu\text{g g}^{-1}$ ) detected in the different sample categories.

	$< 10^2$	$10^2\text{-}10^3$	$10^3\text{-}10^4$	$>10^4$	mean	median	min.	max.
electronics	2	16	14	15	12,300	2620	80	58,900
food-drink	0	14	0	0	410	369	179	893
clothing-upholstery	1	10	3	0	1570	317	90	9922
cleaning-storage	0	3	0	0	355	342	229	495
construction-plumbing	0	11	2	1	1560	407	103	13,000
toys-hobbies	1	17	6	0	1490	571	72	9190
office-stationery	0	6	3	0	855	319	119	2720
leisure-sport	0	7	4	0	775	494	122	2470
vehicle interiors	1	6	7	0	1710	975	61	6020
<b>total</b>	<b>5</b>	<b>90</b>	<b>39</b>	<b>16</b>	<b>4710</b>	<b>559</b>	<b>61</b>	<b>58,900</b>

Figure 1: The spectrum generated by the NDT software for red Christmas beads, illustrating the principal peaks for Sb and Br below 30 keV.

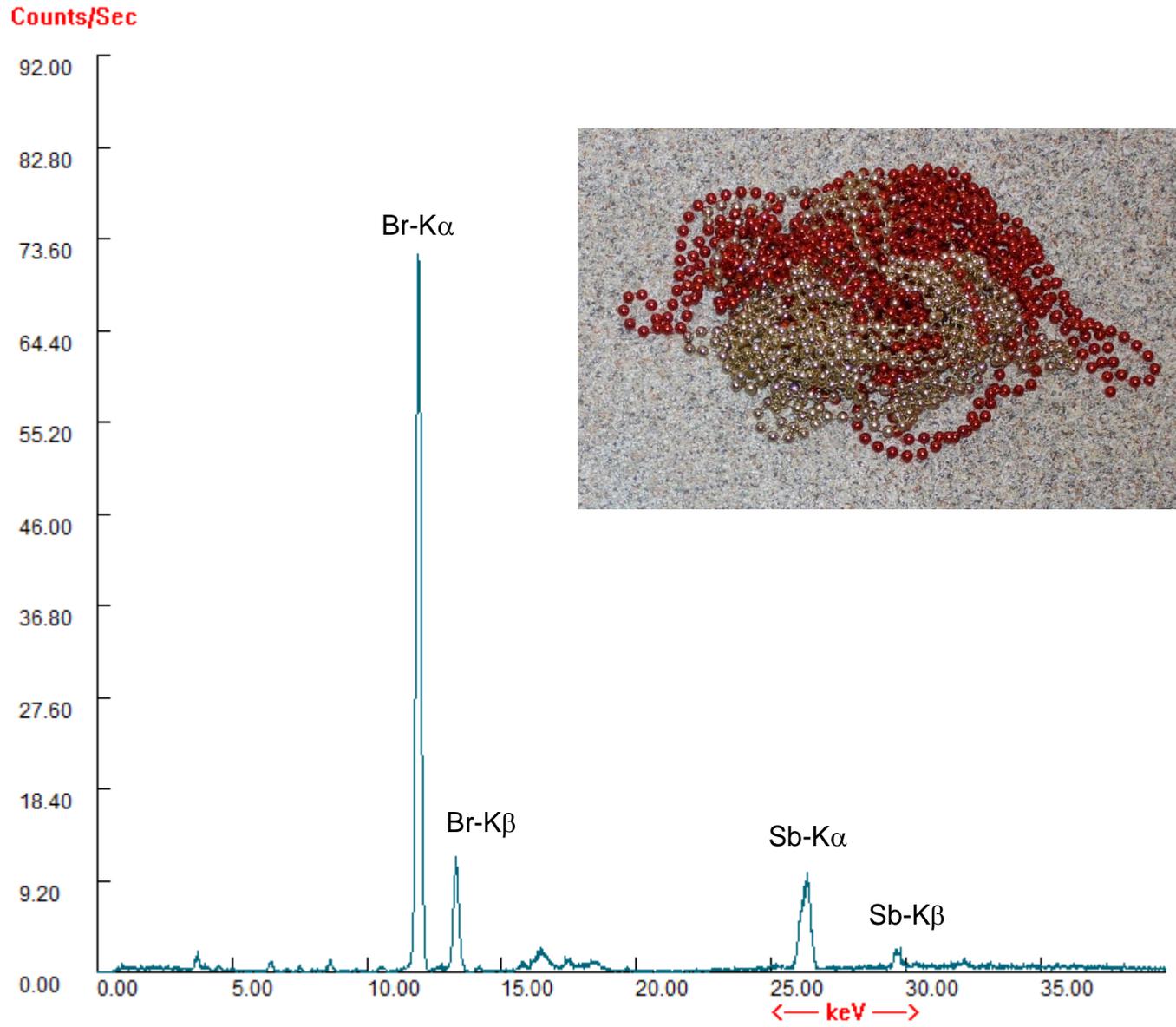
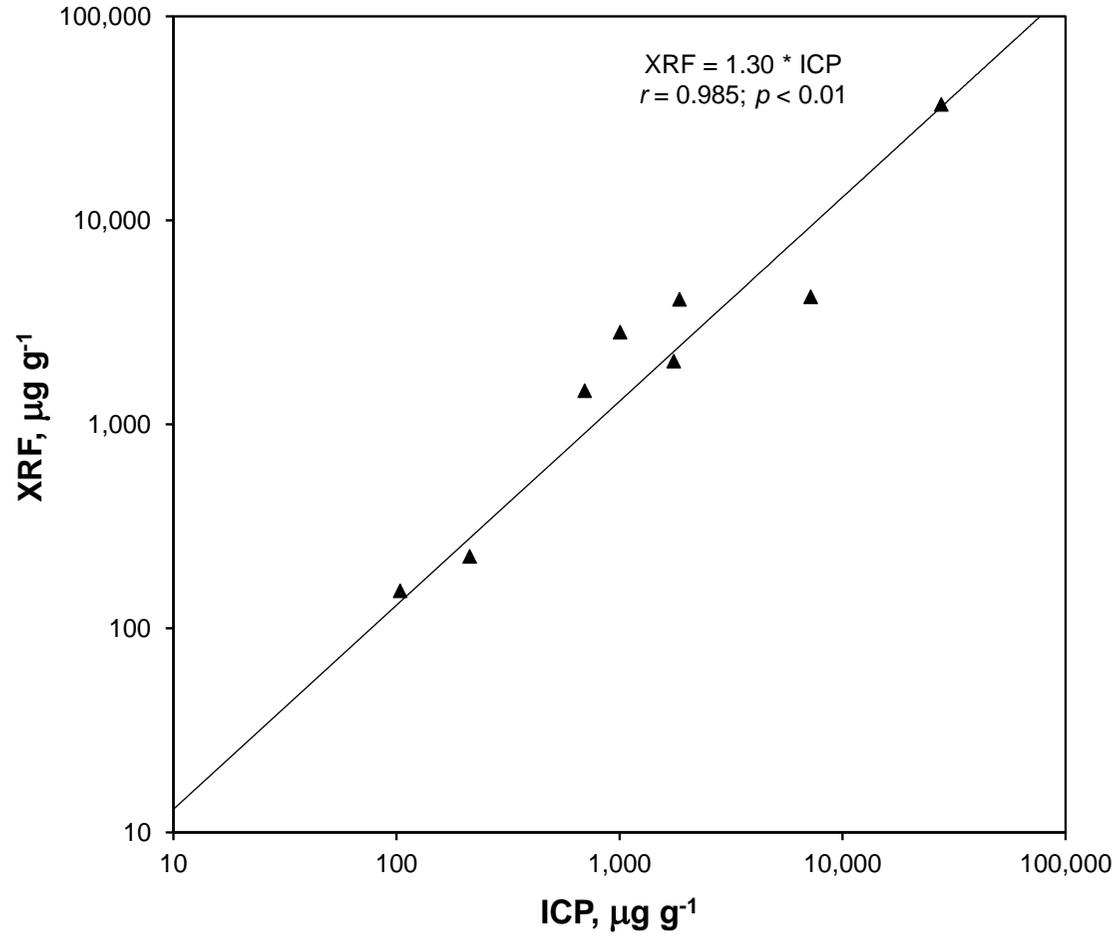


Figure 2: A comparison of the concentrations of Sb in various samples as returned by the FP-XRF and by ICP-OES following acid digestion. Annotated are the best fit line through the data and statistical parameters defining the relationship.



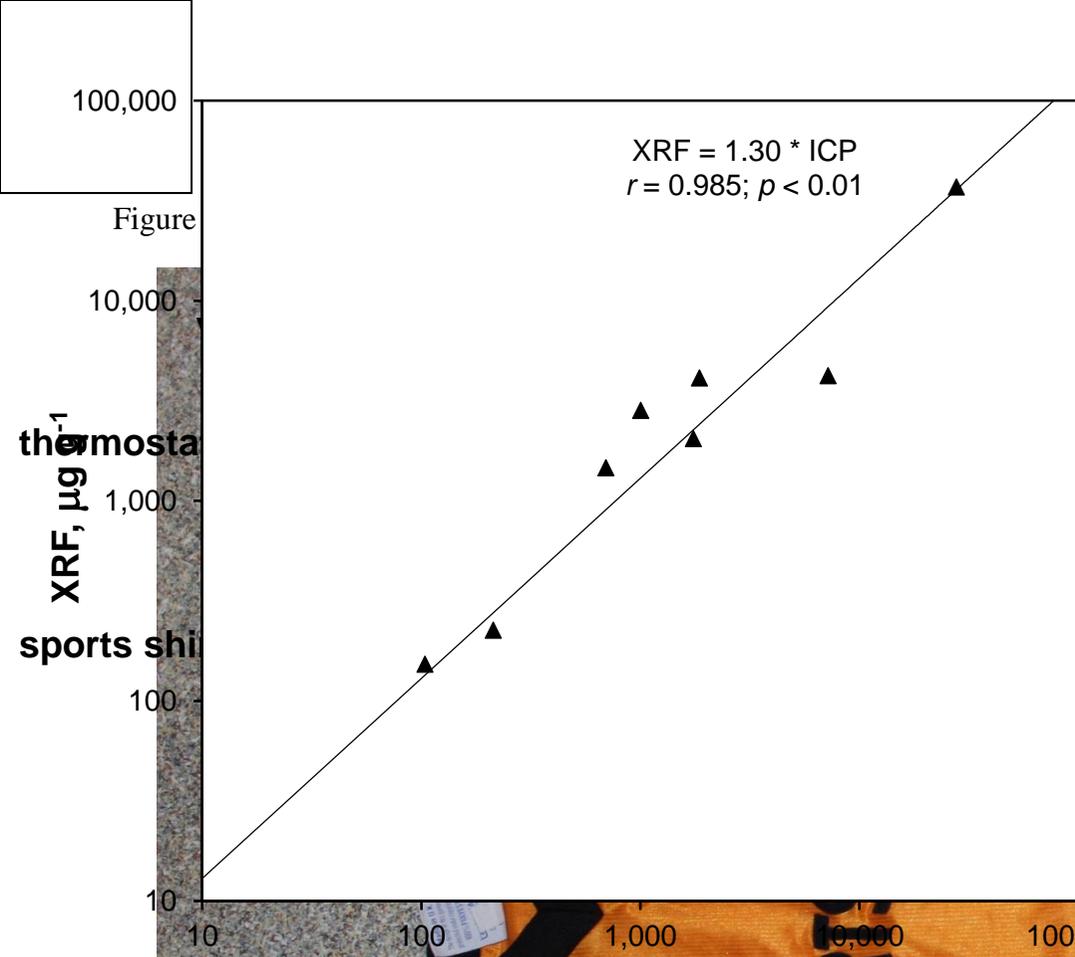


Figure 1: Comparison of XRF and ICP concentrations for various samples. The plot shows a strong positive correlation between the two methods, with the regression equation  $XRF = 1.30 * ICP$  and  $r = 0.985; p < 0.01$ .

