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

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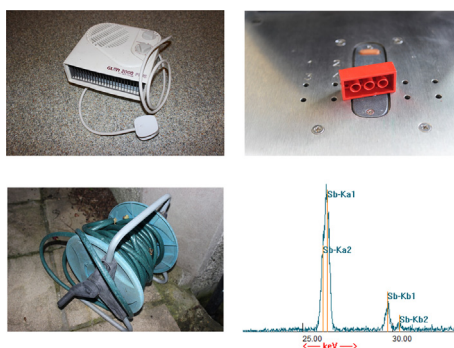
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### HIGHLIGHTS

- Sb has been measured by FP-XRF in over 750 plastic consumer products and components.
- The highest concentrations (several % by weight) were encountered in electronic casings.
- The presence of Sb is attributed to its use as a catalyst and flame retardant synergist.
- Of greatest concern is the presence of Sb in food packaging, drinks bottles and toys.
- There is evidence of electronic casings being recycled into consumer products.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Very little systematic information exists on the occurrence and concentrations of antimony (Sb) in consumer products. In this study, a Niton XL3t field-portable-X-ray fluorescence (FP-XRF) spectrometer was deployed in situ and in the laboratory to provide quantitative information on Sb dissipated in plastic items and fixtures (including rubber, textile and foamed materials) from the domestic, school, vehicular and office settings. The metalloid was detected in 18% of over 800 measurements performed, with concentrations ranging from about 60 to 60,000  $\mu\text{g g}^{-1}$ . The highest concentrations were encountered in white, electronic casings and in association with similar concentrations of Br, consistent with the use of antimony oxides (e.g.  $\text{Sb}_2\text{O}_3$ ) as synergistic flame retardants. Concentrations above 1000  $\mu\text{g g}^{-1}$ , and with or without Br, were also encountered in paints, piping and hoses, adhesives, whiteboards, Christmas decorations, Lego blocks, document carriers, garden furniture, upholstered products and interior panels of private motor vehicles. Lower concentrations of Sb were encountered in a wide variety of items but its presence (without Br) in food tray packaging, single-use drinks bottles, straws and small toys were of greatest concern from a human health perspective. While the latter observations are consistent with the use of antimony compounds as catalysts in the production of polyethylene terephthalate, co-association of Sb and Br in many products not requiring flame retardancy suggests that electronic casings are widely recycled. Further research is required into the mobility of Sb when dissipated in new, recycled and aged polymeric materials.

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### 1. Introduction

One of the main features of the current use of chemical elements is their application in materials at low concentrations by weight but in a

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large variety of items. Measuring trace elements in final products is often challenging but necessary for different reasons, ranging from an assessment of their potential toxicological and ecotoxicological effects to an evaluation of in-use stocks for chemical life-cycle assessments.

In this context, antimony (Sb) is a particularly interesting element for two reasons. Firstly, its use increased significantly in the first decade of the present century (total antimony consumption grew by about 40% and from 147,000 to 206,000 t between 2000 and 2011; USGS, 2016) and, although global production has receded slightly since 2011, it is predicted to increase from 2015 to 2020 (Dupont et al., 2016). Secondly, the type of use of Sb has shifted from applications where it can be recovered (e.g., as an additive in lead alloys) to those where recycling is not possible because of its dissipation in the product (e.g., as a catalyst in polyethylene terephthalate (PET) manufacturing and as a synergistic flame retardant) (Zimmermann and Gößling-Reisemann, 2013; Talens Peiró et al., 2013; Ciacci et al., 2015). At present, Sb use as a catalyst and flame retardant accounts for about 60% of its total production while applications in metallurgy account for about 35% (Schwarz-Schampera, 2014).

Despite the cumulative toxicity of Sb and its similarity with As in many biological respects, the element was rather poorly studied until the mid-1990's. Specifically, a possible link between sudden infant death syndrome (SIDS) and volatile antimony hydride generated via the biomethylation of antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) used as a flame retardant synergist in cot mattress covers triggered a strong interest in the metalloid (Richardson, 1990, 1994). More recently, scientific and media attention has been diverted to the presence of measurable concentrations of antimony in bottled water (Shotyk et al., 2006; Westerhoff et al., 2008), fruit juices (Hansen and Pergantis, 2006) and ready-meals (Haldimann et al., 2013) arising from the leaching of Sb from PET containers. PET is a highly favourable and widely used material for food and drink packaging and oven-proof and reheatable meals because of its thermal and physical stability, low density and recyclability (Chapa-Martinez et al., 2016).

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

## 2. Materials and methods

### 2.1. Material access, collection and categorisation

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

Depending on their location and principal use, samples were categorised according to the list given in Table 1. However, it must be

appreciated that several of the categories are not mutually exclusive (for example, electronic toys, constructed versus upholstered flooring, and storage for food and for sports equipment) and that some samples comprised distinct components that were analysed and categorised separately. While the surface or coating of most samples was targeted, occasional end-of-life electronic products were dismantled and interior components analysed individually.

### 2.2. XRF analysis

Samples were analysed by energy-dispersive FP-XRF using a Niton XL3t 950 He GOLDD+ that was employed handheld and in situ or configured in the laboratory in an accessory-stand. The Niton XL3t employs a miniature X-ray tube with a silver transmission anode that operates at up to 50 kV of high voltage and 200  $\mu\text{A}$  of current and is fitted with a geometrically optimised large area silicon drift detector to detect fluorescent X-rays from the sample. The concentrations of Sb, based on characteristic peaks at 26.359 KeV ( $\text{K}\alpha$ ) and 3.604 KeV ( $\text{L}\alpha$ ) (Fig. 1), were determined in a 'plastics' mode through a standardless, fundamental parameters-based alpha coefficient correction model. This iterative approach accounts for background matrix effects by describing characteristic X-ray intensities using mathematical equations that tie together the physics of the interaction of X-rays with sample components, and has a wide dynamic range that is independent of the size and shape of the surface (Bosco, 2013). Concentrations of Br and Cl were also recorded during sample analyses as indicators of the presence of halogenated flame retardants and polymer chlorination (and polyvinyl chloride, PVC).

Because plastics are composed of light elements that are weak absorbers and relatively strong scatterers of X-rays, below a critical thickness the measured intensity of characteristic X-rays will be dependent on both the analyte concentration and the depth of the sample. For polyethylene, for example, the critical thickness is about 9 mm while for PVC the presence of chlorine results in a corresponding thickness of around 5 mm; for polymers containing heavier elements, including Sb and Br, critical thickness depth is reduced compared with that of the pure material. In the plastics mode, the Niton XL3t incorporates a thickness correction algorithm down to 50  $\mu\text{m}$  that employs a compensation for mass absorption based on Compton scatter so that variations in density are factored in. Although the corrective algorithm is embedded in the fundamental parameters code and inaccessible to the user, it has been empirically defined for a number of elements (including Sb, Br and Cl) and in a variety of plastics elsewhere (Turner and Solman, 2016).

In the present study, sample thickness was determined through the flattest or smoothest ('measurement') surface using 300 mm Allendale digital callipers, and to increase the effective depth and flatness of thin or hollow samples analysed in the accessory stand, items were cut (with scissors, pliers or a blade), folded or layered. The corrective algorithm was employed for all samples whose measured thickness was <30 mm, while an estimated value was applied to all objects and components whose interiors were inaccessible or that were fixed to or components of walls, floors, windows, doors and appliances. A thickness of 0.05 mm was assumed when analysing painted surfaces or paints and cosmetics that had been applied to glass slides and oven-dried (at 40 °C for 12 h).

In the laboratory, the XRF was employed nose-upwards in a collapsible bench-top accessory stand (Thermo Scientific SmartStand, with internal dimensions of 20 cm  $\times$  20 cm  $\times$  10 cm; PN 420-017) and was connected to a laptop computer via USB. Samples were placed on the stainless steel base plate of the accessory stand above the detector window or, for samples smaller than the 8 mm window diameter, on to a SpectraCertified Mylar polyester 3.6  $\mu\text{m}$  film that was carefully positioned such that the sample lay centrally above the window. On closing the shield of the stand, measurements with appropriate thickness correction and collimation (3 mm or 8 mm beam width) were activated

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