

## DEVELOPMENT OF A NON-DESTRUCTIVE TESTING STRATEGY TO RAPIDLY IDENTIFY PBDEs IN CONSUMER PRODUCTS

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### Introduction

There is growing international concern surrounding human exposure and environmental release of certain chemicals previously incorporated into consumer products. In May 2009, nine new compounds were added to the Annexes of the Stockholm Convention on Persistent Organic Pollutants (POPs), including three compounds that are known to have been added to a wide range of consumer products. In this paper, the investigation of one of these POPs - commercial octabromodiphenyl ether (c-octaBDE) – in consumer products will be discussed. C-octaBDE is an additive flame retardant (i.e. not chemically bonded to the polymer) that has been used in a range of consumer products including the casings of computers, televisions and other home appliances. Typically, c-octaBDE is added at a weight loading of 12 – 18% (UNEP, 2007). Unlike chemically bonded flame retardants, PBDEs may escape from the polymer into the environment through a number of pathways including blooming, weathering and wearing of the product (dust) during the service life of the product, and be leached from product to landfill (Allen et al, 2008; Osako et al, 2004).

Despite bans and restrictions on the production and use of c-octaBDE in many countries (including Australia) as early as 2004, it is reasonable to assume that c-octaBDE may still be entering Australia in the plastic components of imported products. Understanding the level of presence of c-octaBDE in consumer products that are currently imported into Australia is an important consideration in deciding whether to initiate a strategy to mitigate/control the release of c-octaBDE to the Australian environment.

The specific aims of this study were to 1) develop a rapid, non-destructive screening strategy to identify c-octaBDE in a broad range of consumer products; 2) compare the results of the non-destructive testing with quantitative chemical analysis and 3) provide an indication of the number and types of products entering Australia that may contain c-octaBDE. Furthermore, this work aims to enhance the suite of testing methods established internationally for the rapid, cost-effective detection of such chemicals

### Materials and methods

The study is comprised of three components: (1) general screening for bromine-containing compounds, including BFRs using an X-ray fluorescence hand-held device (XRF device), (2) development and application of a surface wipe test to screen for specific BFRs (including PBDEs) and (3) destructive chemical extraction and quantitative analysis of PBDE concentrations in consumer products.

**XRF Screening** A handheld Niton XRF device (ThermoFisher) was used to provide an estimation of bromine concentration in the scanned area of an item presented as ppm (i.e. 1000 ppm equivalent to 0.1% w/w of bromine). The XRF device was held to the surface of the product and a measurement triggered for between 30 and 60 seconds in 'Plastics Mode'. Details attributed to the product such as the specific area of the product tested, model number, product name and country of manufacture were recorded. For many products, multiple XRF measurements were taken to target areas where heat was specifically generated, where different plastics were used and products were made of multiple components (for e.g. control panel, external plastic on microwave door, plastic on inside of microwave door). A two point calibration was regularly performed throughout the analyses using internationally certified standards of low and high-level bromine-containing polyethylene (Institute for Reference Materials and Measurements (IRMM), Belgium). To eliminate the possibility of contamination from

PBDE-containing dust particles, any visible dust was removed from the surface of the item prior to measurement with a dry KimWipe (Kimberley Clark).

**Swipe test method** The selected area was wiped free of surface dust using a KimWipe wetted with MilliQ water and wiped dry. Where possible, the selected area was approximately 100 cm<sup>2</sup>. A solvent rinsed Whatmann filter paper wetted with isopropanol. The filter paper was firmly wiped in concentric circles towards the middle of the area, refolded and the fresh side also used to wipe the area free of solvent. The filter paper was placed in a solvent-rinsed amber glass bottle and any remaining solvent removed under a gentle stream of nitrogen. 10 mL of dichloromethane was added to each of the bottles and shaken at 100rpm at room temperature for 2 hours, before being placed in an ultrasonic bath for 5 minutes. The extracts were filtered through a 0.20 µm PTFE syringe filter and the filtrate blown down at 40° C under a gentle stream of nitrogen. The concentrated extracts were transferred to a 2 mL vial and adjusted to a final volume of 200 µL in methanol for analysis. Chemical analysis was performed using a HPLC (Shimadzu) coupled to a 5500 Q-Trap mass spectrometer (AbSciex) equipped with an atmospheric pressure chemical ionization (APCI) source. Separation was performed using a Gemini C18 3µm 2mm x 50mm with Gemini C18 3µm guard column, and samples were quantified by external calibration.

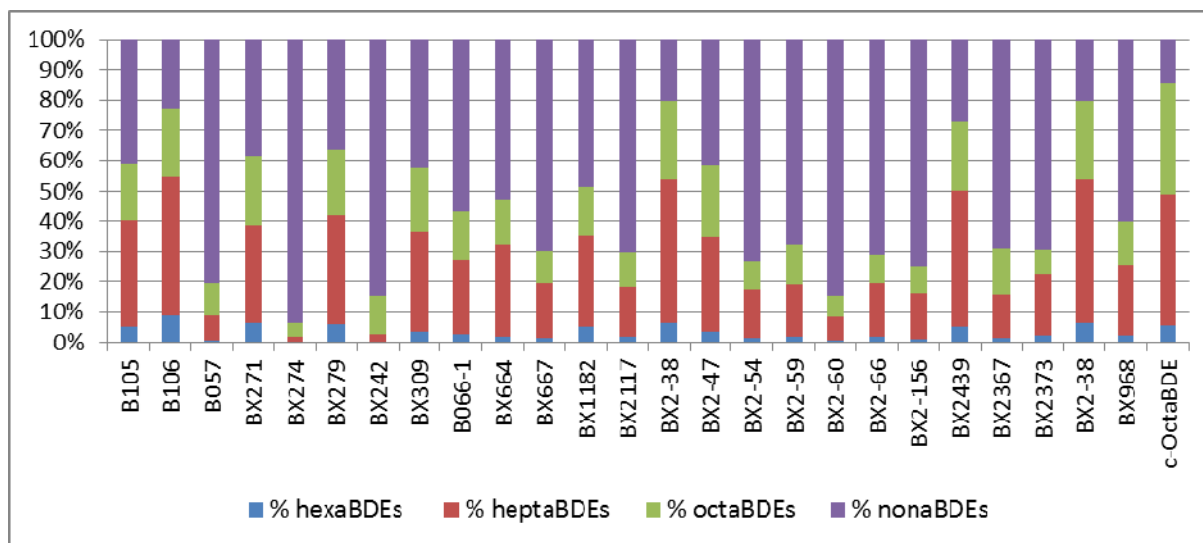
**Destructive testing** Products selected for quantitative analysis for PBDEs and other selected BFRs were sent to the VU University Amsterdam. Approximately 1 gram of plastic was finely ground, extracted in an organic solvent, subjected to clean up on a silica column and analysed by electron capture negative ionization technique and mass spectrometry detection (GC/ENCI-MS) as previously described (De Boer et al. 2001, 2006).

## Results and discussion

A total of 1714 XRF measurements were taken from plastic products and product components manufactured in approximately 40 different countries (including Australia). Products were selected for XRF screening based on the criteria: to represent a broad range of product types (i.e. toys, large household appliances, televisions, car accessories); were recently imported and currently in use; represent a large market share and were accessible to analyse in store.

From the 1714 products pre-screened for bromine-containing compounds (and the possible presence of c-octaBDE) using the XRF, 149 products were selected for swipe testing to confirm the presence of specific BFRs (including PBDEs). Products were chosen for swipe testing based on the following criteria: a high bromine reading measured by XRF (>50 000 ppm); they represent a broad range of product types; and they were to include a selection of products that recorded a range of bromine concentrations from XRF measurements (1000 – 50 000ppm) and a selection of products that recorded no detectable bromine content from XRF to validate the XRF method. Whilst XRF data provided an initial indication of the possible presence of BFRs, the procedure is unable to distinguish bromine containing compounds. As c-octaBDE is a mixture of many hexa- to nona-brominated PBDE congeners, the two main congeners of the c-octaBDE mixture BDE-183 and BDE-197, were chosen as ‘markers’ for the presence of c-octaBDE

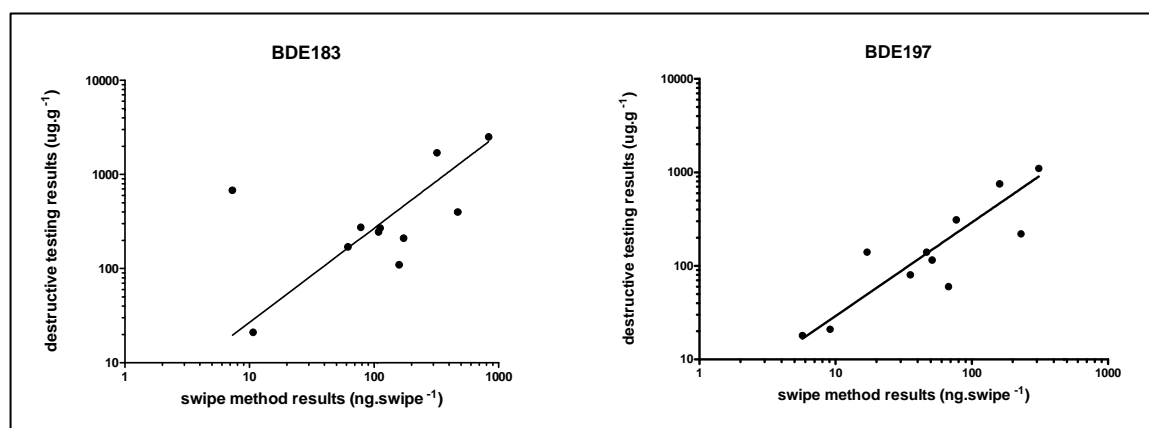
Figure 1 presents the 25 product swipes that detected the highest amounts of the two congeners, strongly indicating the possible presence of the c-octaBDE mixture. The proportion of hexa- to nona- congeners (excluding other congeners and BFRs) detected in the swipes is compared to the composition of the c-octaBDE mixture. Despite the presence of c-octaBDE congeners, BDE-209 (decaBDE) still remained the dominant PBDE present in the swipe tests, contributing 51 - 94 % of the total amount of PBDEs detected. In addition, other BFRs such as hexabromocyclododecane (HBCD) and tetrabromobisphenol (TBBPA) were also present. The high proportion of BDE-209 and other BFRs compared to the hexa- to nona-PBDE congeners initially suggest that the amount of c-octaBDE present was low.



**Figure 1 PBDE profiles (excludes BDE-209) of swipe results of products that contained c-octaBDE congeners compared to the composition of c-octaBDE (UNEP, 2007)**

Based on the swipe test results, 16 of these 25 products were selected for further destructive testing and quantitative analysis of PBDEs. From the, albeit low, concentrations of BDE-183 and 197 detected, the concentration of the c-octaBDE mixture could be estimated by dividing the sum of the two congeners by the fraction they occur in the c-octaBDE mixture (0.59). Similarly to the swipe tests, BDE-209 and TBBPA were the most frequently detected and abundant BFRs.

To investigate if the swipe method could be used to predict the c-octaBDE content of plastics, the results of the swipe test (ng per swipe) were compared to the results of the destructive testing ( $\mu\text{g}\cdot\text{g}^{-1}$ ) (Figure 2). Using this relationship, the concentration of c-octaBDE present could be estimated from the swipe test. Ratios between the swipe test method and the destructive testing method for the estimation of c-octaBDE ranged between 0.32 and 3.8 with an average of 1.3. Further work to standardize the amount of solvent used and pressure and time applied would improve this correlation. In the broader study we conducted, samples that had no bromine detected by XRF but had a positive swipe test had insignificant amounts of BFRs measured during destructive testing. These levels were within the range of analytical error for the XRF instrument, and these false positives occurred in <10% of samples.



**Figure 2 Correlation of the results of two c-octaBDE congeners using the swipe test method and destructive testing**

The combined non-destructive strategy of pre-screening by XRF followed by a swipe test allowed the successful rapid and cost effective identification of products that contain c-octaBDE. Using the three tiers of data gathered in this study we are able to: (1) Identify the types of products that contain BFRs and more specifically, the BFR signatures of certain product types; (2) identify specific plastic products which contain the indicators c-octaBDE using non-destructive test methods (combined XRF and swipe test method) with a high degree of certainty; (3) identify the types of products that would most likely contain c-octaBDE; (4) identify countries which typically manufacture and/ or export products containing c-octaBDE and conclude that the likely source of c-octaBDE entering the country is through the use of plastic recyclate manufactured into new consumer products. Overall, we have demonstrated that the combined non-destructive methods of XRF and swipe testing are powerful tools for identifying key BFRs and more specifically, estimating the c-octaBDE content in consumer products.

The full findings referred to in this study are currently being considered by the funding body (Australian Government) for possible public release. It is anticipated that all necessary approvals will be granted for presentation of the finalized data at Dioxin 2013.

### **Acknowledgements**

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