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# Antimony release from polyester textiles by artificial sweat solutions: A call for a standardized procedure

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## ABSTRACT

Polyester fibres are usually contaminated by antimony because of its use as a catalyst in the production of polyethylene terephthalate and as a flame retardant synergist in a variety of new and recycled polymers. The present study determined the release of antimony (at total concentrations ranging from about 125 to 470  $\mu\text{g g}^{-1}$ ) from polyester textile samples designed to be in contact with human skin using standard artificial sweat solutions (ISO 105-E04 and EN 1811). The study also examined the role of different experimental parameters on the release of the metalloid. Overall, and using the default parameters, between about 0.05 and 2% of total antimony (or 0.1–1  $\mu\text{g g}^{-1}$ ) was mobilized into artificial sweat. A reduction in time (from 24 to 12 h) and temperature (from 37 to 20 or 4 °C) and an increase in pH (from 5.5 to 7) resulted in a decline in antimony mobilization from textiles, while altering textile mass to solution volume and the presence of lactate had little impact on the results. Removal of a filtration step increased antimony mobilization but this was attributed to artefacts associated with release from microfibrils during extract storage and analysis. In general, antimony mobilization was sufficiently repeatable using either EN 1811 or ISO 105-E04 but the latter is recommended for an assessment of antimony mobilization and potential exposure because its pH is closer to that of human sweat. Since the first fraction of either extractions mobilized the greatest quantity of antimony, exposure can be minimized by washing articles before use.

## 1. Introduction

In 2018, 62% of the world's fibre production (107 Mt) was synthetic, with polyester having a share of around 51.5% of the total production (Textile Exchange, 2019). Polyester is used in apparel as well as in home furnishings, automotive interiors and construction materials. Polyethylene terephthalate (PET) is the most common type of polyester used in textiles and antimony is present in 80–85% of all virgin PET because antimony compounds (mainly  $\text{Sb}_2\text{O}_3$ ) are used as catalysts in its production. Antimony can also be present in fabrics due to its use as a synergist of halogenated flame retardants. Antimony trioxide is, however, a suspected carcinogen for humans (NTP, 2018).

Although there is ample evidence that clothing influences human exposure to chemicals, only a few studies have quantified this route of exposure by direct measurements (Licina, 2019). Significantly, the potential release of antimony in textile polyesters has not been substantially questioned from a toxicological point of view and available

information is often buried in grey literature (Laursen et al., 2003; Bundesinstitut für Risikobewertung, 2012) or reported among other elements in a few peer-reviewed articles (e.g. Rovira et al., 2017; Herero et al., 2019). This is in stark contrast to the attention paid to antimony release from PET containers used to store food and drink (Filella, 2020).

There is no regulatory limit on antimony concentrations in polyester apparel or textiles used in furnishings. Antimony content is, however, considered for the award of the European Union Ecolabel for textile products and should not exceed 260  $\mu\text{g g}^{-1}$  in the polyester fibres (European Commission, 2014). The test should be carried out on a composite sample of raw fibres prior to any wet processing, although polyester fibres manufactured from recycled PET bottles are derogated from this requirement. By comparison, the OEKO-TEX® STANDARD100 label requires that extractable antimony is less than 30  $\mu\text{g g}^{-1}$  for clothing textiles (OEKO-TEX Association, 2020).

Migration tests with artificial sweat are commonly used to test for

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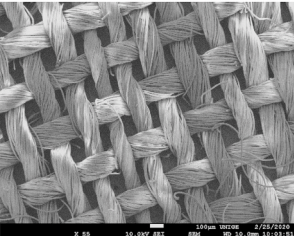
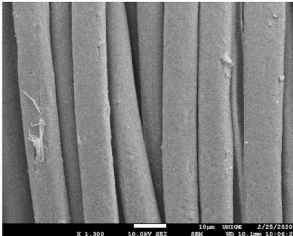
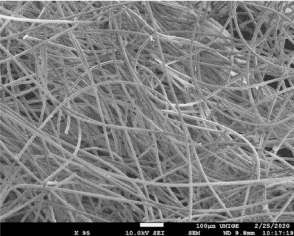
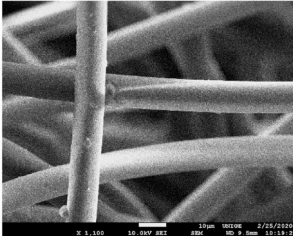
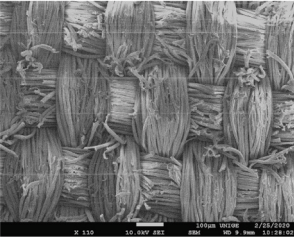
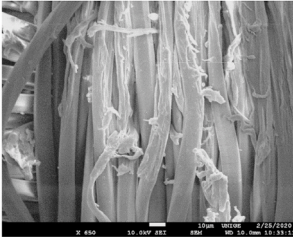
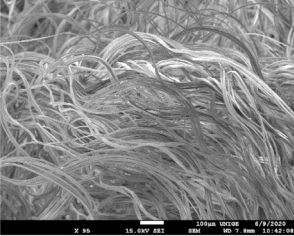
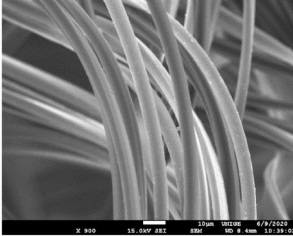
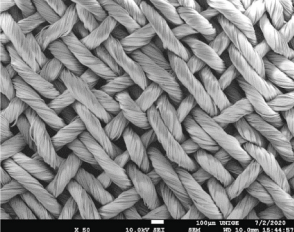
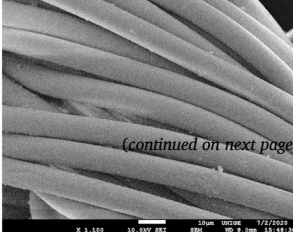
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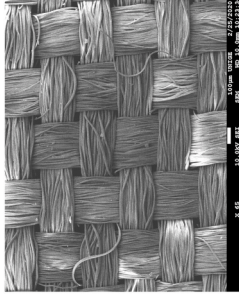
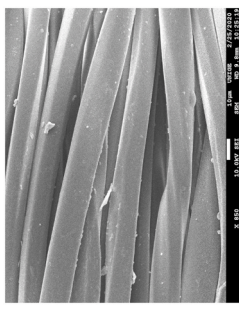
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**Table 1**  
 Details of the samples tested in the present study. Total antimony was determined by XRF and extractable antimony was determined according to ISO 105-E04, with three 24-h sequential extractions at 37 °C. All samples were purchased new except OMS.

Sample identifier	Sample description	Sample origin	Year of purchase	Total Sb in fabric / $\mu\text{g g}^{-1}$	Sb extracted/ $\mu\text{g g}^{-1}$	Sample SEM images	
						White line: 100 $\mu\text{m}$	White line: 10 $\mu\text{m}$
OMS	Old, blue men's shirt	Spain	Unknown	471	$0.402 \pm 0.128$		
PFB	Blue 'polar fleece' blanket OEKO-TEX certified	Baumarkt, Luxembourg	Nov 2019	185	$0.904 \pm 0.121$		
STP	Men's swimming trunks	Primark, Plymouth, UK	Jan 2020	286	$0.480 \pm 0.126$		
TWY	'Twido Household' microfibre cleaning cloth, yellow 88% polyester, 12% polyamide	Luxembourg Made in PRC	March 2019	125	$2.572 \pm 0.031$		
WSP	Women's shirt	Primark, Plymouth, UK	Jan 2020	357	$2.477 \pm 0.093$		

(continued on next page)

Table 1 (continued)

Sample identifier	Sample description	Sample origin	Year of purchase	Total Sb in fabric / $\mu\text{g g}^{-1}$	Sb extracted/ $\mu\text{g g}^{-1}$	Sample SEM images
WUC	White pillowcase with unicorn design OEKO-TEX certified	Baumarkt, Luxembourg Made in Turkey	Nov 2019	452	$0.689 \pm 0.154$	 

colour fastness to perspiration and are usually based on well-established protocols designed to examine metal release from items like jewellery (Midander et al., 2016). The test most commonly cited for textiles is the ISO 105-E04 (ISO, 2013) but, in practice, the literature referring to this approach, including OEKO-TEX (2018), state the composition of the synthetic sweat but then apply a variety of non-standardized procedures for the extraction itself. Studies claiming to use the AATCC test method TM015 (AATCC, 2013) and European Standard EN 1811 (BSI, 2011), both of which contain lactate, a strongly coordinating ligand which is naturally present in human sweat, also appear to adopt a variety of experimental protocols.

Given the likely dependence of chemical extraction on the composition of artificial sweat solution and the absence of any standardized experimental protocol, we used the procedure described by Herrero et al. (2019) and tested the effects of different parameters on antimony release from polyester fibres. The parameters studied included extractant solution composition and pH, temperature, duration, number of extraction steps, sample to extractant ratio, and effects of filtration. Synthetic sweat solutions differ in their prescribed pH, with AATCC TM015 carried out at pH 4.3, ISO 105-E04 usually using pH 5.5 but sometimes using pH 8 (Matoso and Cadore, 2012), and EN 1811 employing pH 6.5. We used the acidic version (pH 5.5) of ISO 105-E04 and explored the change in extraction behaviour when its pH was increased or decreased by 1.5 units. In an effort to choose samples designed to come into dermal contact during normal use, we worked on old (30+ years) and new articles of clothing (shirts and swimming trunks) and items for general household use (a microfibre cleaning cloth and blanket) made of polyester fibres and as described in Table 1. Samples were inspected by scanning electron microscopy (SEM) and their antimony content was measured by X-ray fluorescence (XRF) spectroscopy. Antimony concentrations were in the range found in our extensive survey of the metalloid amongst clothing items in consumer and plastic products (antimony detected in 32 out of 63 samples analysed; concentration range: 44–476  $\mu\text{g g}^{-1}$ ; median: 146  $\mu\text{g g}^{-1}$  (Turner, 2019).

We emphasize that the aim of the present article is not to study as many different polyester fabrics as possible (hence the restricted number of samples) but rather to highlight the potential problem of the presence of antimony in fabrics and its mobilization from them, hitherto ignored by regulatory authorities, and the difficulties arising from the use of unclear, undisclosed or arbitrarily selected protocols. Regarding the latter, there is a clear need for procedural standardization that regulating authorities must address.

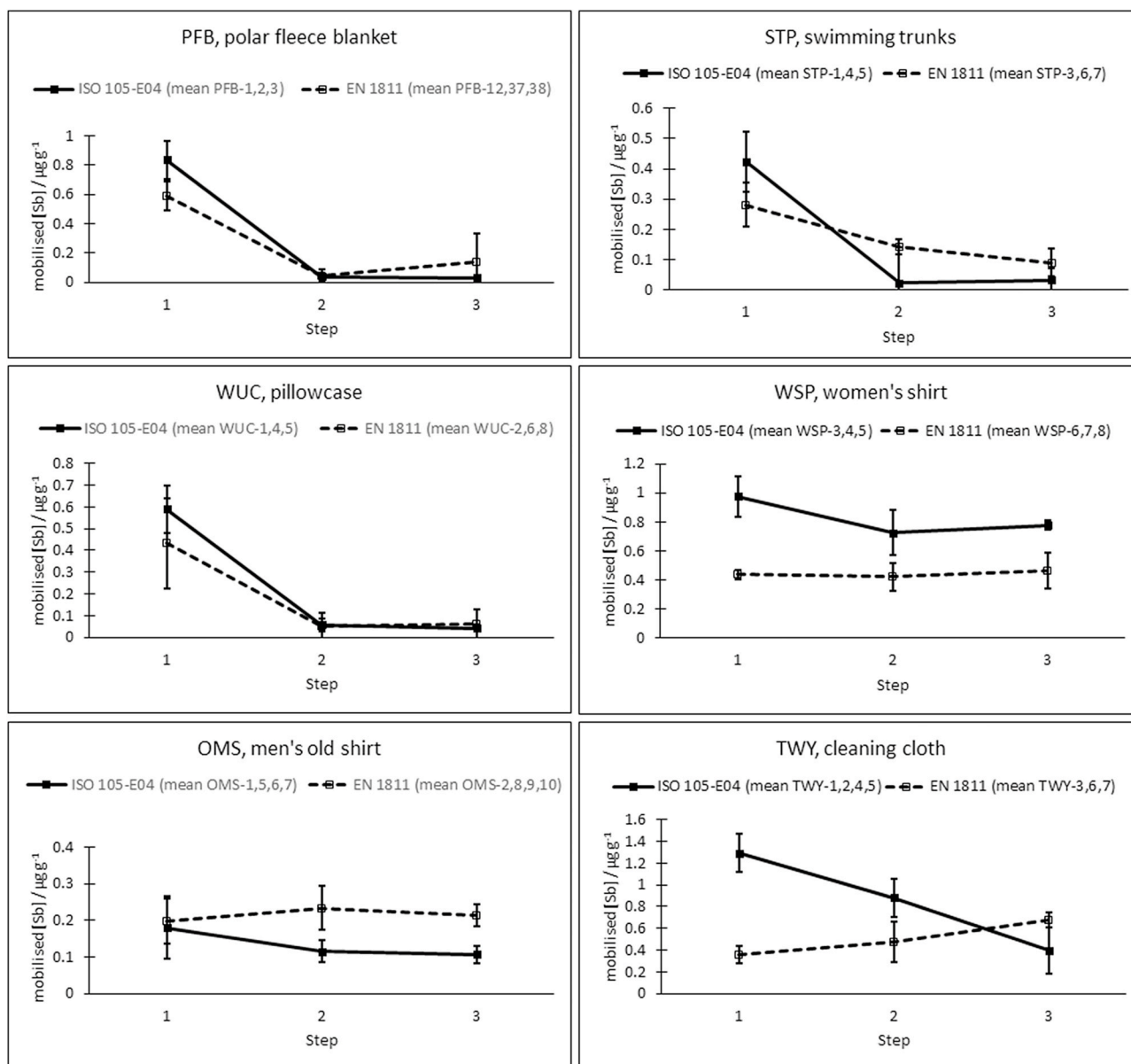
## 2. Materials and methods

### 2.1. Textile samples

Six polyester textile samples, acquired in the European Union (but not necessarily manufactured there) and described and coded in Table 1, were selected for study. These consisted of five new products and one used item, and three articles of clothing, a pillowcase, a fleece blanket and a microfibre cloth.

### 2.2. Measurement of antimony by XRF

The samples were analysed for antimony by energy-dispersive FP-XRF using a Niton XL3t 950 He GOLDD + operated in an accessory stand. Material was folded and compressed above the detector window and counted in a standardless 'plastics' mode with thickness correction. Counting was undertaken for periods ranging from 30 to 180 s, depending on sample thickness, that were distributed equally or in a 1:2 ratio between a low energy range (20 kV and 100  $\mu\text{A}$ ) and main energy range (50 kV and 40  $\mu\text{A}$ ). Spectra were quantified by fundamental parameter coefficients to yield concentrations on a dry weight basis (in  $\mu\text{g g}^{-1}$ ) and with a counting error of  $2\sigma$  (95% confidence). As a performance check, polyethylene reference disc Niton PN 180–619 (Sb



**Fig. 1.** Extraction results by ISO 105-E04 and EN 1811 through three sequential steps (error bars reflect 95% confidence intervals, 3 to 4 replicates as indicated in the legends).

concentration:  $94 \pm 10 \mu\text{g g}^{-1}$ ) was analysed at regular intervals throughout each measurement session.

### 2.3. SEM observations

A JEOL JSM-7001F scanning electron microscope was used for sample observations. Cloth samples were mounted on aluminium stubs using double-sided conductive carbon tape and sputter-coated with Au (ca. 10 nm).

### 2.4. Sample extraction preparation

For the extractions, cloth samples were laid on a flat surface and cut to squares of approximate dimensions 2 cm by 2 cm using a pair of stainless steel tailor's scissors. Approximately 1 g of material was weighed and rinsed by brief immersion in about 200 mL of Millipore Milli-Q water (MQW) to remove any superficial dust before being air-dried on clean filter paper. Throughout the procedure, samples were handled using glass rods and ceramic tweezers (Vomm, Germany).

### 2.5. Artificial sweat solutions

Three artificial sweat solutions were used:

- Solution ISO 105-E04 (ISO, 2013). This was made by dissolving 92.5 mg of histidine (Cellpure,  $\geq 99\%$ , Roth, Germany), 1.25 g of sodium chloride (p.a., Roth) and 0.55 g of sodium dihydrogen phosphate dihydrate (p.a., Roth) in about 200 mL of MQW, adjusting the pH of the solution to 5.5 with  $0.1 \text{ mol L}^{-1}$  hydrochloric acid (Supra, Roth) under potentiometric control and completing the volume to 250 mL in a volumetric flask.
- Solution ISO 105-E04 + lactate. This solution contained exactly the same compounds and in the same concentrations as the solution above but was supplemented with  $0.014 \text{ mol L}^{-1}$  lactic acid (J. Bourret, France) and adjusted to pH 5.5.
- Solution EN 1811. This was made by dissolving 0.25 g of urea (p.a., Roth), 1.25 g of sodium chloride and 2.8 mL of  $1 \text{ mol L}^{-1}$  lactic acid in 200 mL of MQW and adjusting the pH to 6.5 using  $1.0 \text{ mol L}^{-1}$  and

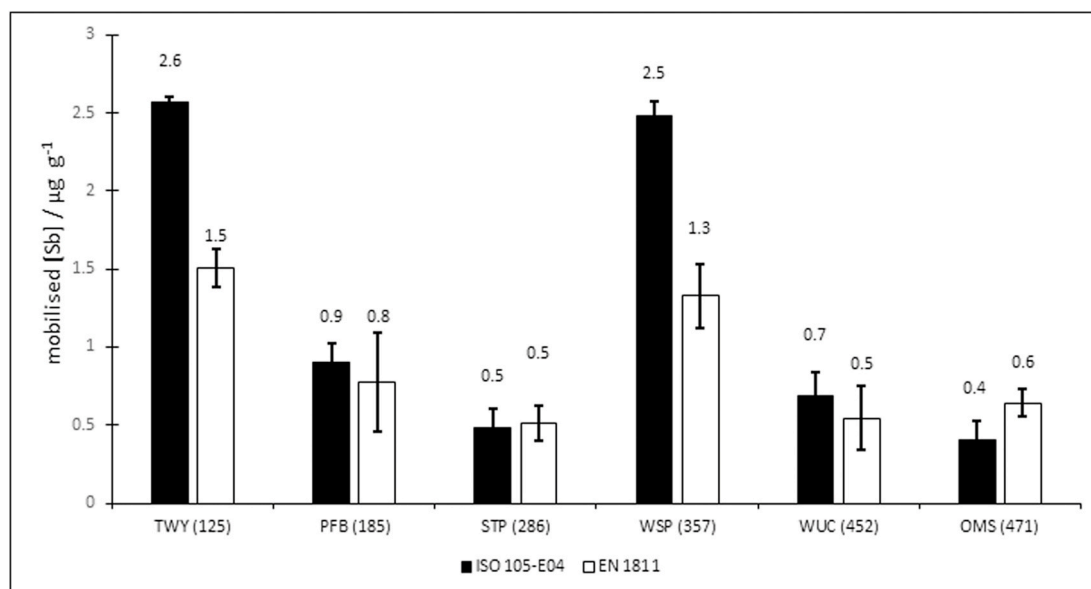


Fig. 2. Cumulated extraction (sum of three stages) for ISO 105-E04 and EN 1811. The error bars define 95% confidence intervals. The total antimony content (in  $\mu\text{g g}^{-1}$ ) is shown in parentheses.

0.1 mol L<sup>-1</sup> sodium hydroxide (p.a., Roth) and completing the volume to 250 mL in a volumetric flask.

All solutions were kept in sterilized, colourless HDPE bottles (Nalgene, US) at 4 °C and used within 3 days of preparation to minimize contamination by bacterial and fungal growth (especially in the presence of lactate). The solution pH was measured with a SevenCompact S220 meter from Mettler Toledo (US, Switzerland) and a Ross (US) combination electrode. The meter was calibrated in the acidic domain using commercial buffer solutions from Hanna (Romania) with known temperature coefficients.

All glassware and HDPE bottles intended for reagent storage were cleaned by sonication (45 min at 50 °C with 180 W power) in a commercial, strongly acidic detergent formulation (Elma 60, Roth). Past experience has shown that this treatment successfully removes any Sb contamination. The PP centrifuge tubes, syringes, stoppers and disposable pipette tips were used as supplied.

## 2.6. Extraction procedure

Approximately 1 g of air-dried material was weighed accurately (to 0.1 mg) into a clear 50 mL polypropylene centrifuge tube with a conical bottom and screw cap (Roth) and 25 mL of artificial sweat solution was added by glass pipette. The tube was shaken to make sure the sample was entirely soaked and immersed in the solution before being placed in a water bath kept at 37 °C. After the desired length of time, the extractant was withdrawn using a 10 or 25 mL polypropylene syringe fitted with a 0.1  $\mu\text{m}$  PVDF filter (Merck Millipore, Ireland) via a 7 cm steel cannula (Brown). Syringes were stoppered with Luer combination caps (Fresenius, Germany) and stored at room temperature pending analysis (within a few days). Some samples were re-analysed after 4 months of storage at room temperature and found to be stable. Meanwhile, a fresh 25 mL portion of extractant was pipetted into the centrifuge tube and the tube returned to the water bath for the next extraction step. Typically, three successive extracts were collected in each experiment. Because it was not possible to drain the tube and the cloth contained in it completely, at every addition/withdrawal step the centrifuge tube was carefully wiped dry on the outside and weighed to keep track of the exact volume of extractant that had been used and carried over from the preceding step.

Solutions that had been in contact with the used sample contained

Table 2

Variations in the protocol compared to the standard protocol (3 successive extractions: 24 h, 48 h, 72 h; at 37 °C with ISO 105-E04 solution, sample = PFB, except where stated otherwise). Differences (Y = yes, N = no) are based on a probability of <0.05 according to a series of paired *t*-tests and with *n* degrees of freedom.

Tested variation of protocol	difference	<i>p</i>	<i>n</i>
12 h sampling intervals instead of 24 h	Y	$3.19 \times 10^{-2}$	4
PFB – no filtration	N	0.718	5
STP – no filtration <sup>a</sup>	N	0.397	4
TWY – no filtration <sup>a</sup>	N	0.308	6
Lower temperature (ambient, ~ 20 °C)	Y	$3.93 \times 10^{-4}$	5
Lower temperature (fridge, ~ 4 °C)	Y	$2.65 \times 10^{-3}$	4
pH 4	N	0.967	7
pH 7	N	$5.88 \times 10^{-2}$	5
Presence of lactate, pH 5.5	N	0.337	7
Ratio 0.5 g: 25 mL	N	$5.71 \times 10^{-2}$	4
Ratio 1.5 g: 25 mL	N	0.462	4

<sup>a</sup> Comparisons were made with the standard protocol applied to samples STP and TWY, respectively.

traces of surface-active compounds (from previous laundering) that seriously interfered with the voltammetric determination of antimony. Thus, surfactants were photochemically destroyed by irradiating 10 mL solution aliquots in quartz tubes, to which 100  $\mu\text{L}$  of concentrated HCl (supra) and 20  $\mu\text{L}$  of H<sub>2</sub>O<sub>2</sub> (30% p.a., Roth) had been added, by a hard UV source (a 180 W water-cooled Hg vapour lamp from Heraeus, Germany) for 3 h at room temperature.

## 2.7. Measurement of antimony concentrations in the solutions

Because of its superior tolerance of high salt concentrations and its much lower cost, we used voltammetry rather than ICP-MS or ICP-OES to determine of total antimony (Sb(V)+Sb(III)) in the extracts. Differential pulse anodic stripping voltammetry was performed on a VA797 Computrace voltammetric workstation (Metrohm, Switzerland) with a classical three electrode assembly (hanging mercury drop working electrode, a Pt rod as a counter electrode and an Ag/AgCl/KCl 3 mol L<sup>-1</sup> double junction reference electrode) using an established method (Quentel and Filella, 2002). Typically, measurements were made using a mixture of 5 mL of extract and 5 mL of concentrated suprapure

**Table 3**

Difference between the ISO 105-E04 (no lactate) and EN 1811 (with lactate) protocols. Differences (Y = yes, N = no) are based on a probability of <0.05 according to a series of paired *t*-tests and with *n* degrees of freedom.

Sample	Difference	<i>p</i>	<i>n</i>
PFB	N	0.172	4
STP	N	0.446	4
TWY	Y (ISO > EN)	$3.27 \times 10^{-7}$	5
OMS	Y (EN > ISO)	$2.82 \times 10^{-3}$	6
WSP	Y (ISO > EN)	$2.44 \times 10^{-5}$	4
WUC	N	$7.20 \times 10^{-2}$	4

hydrochloric acid, with 3–6 standard additions (5–25  $\mu\text{L}$  each) of 1  $\text{mg L}^{-1}$  antimony solution prepared by dilution of a commercial 1000  $\text{mg L}^{-1}$  atomic absorption standard (Alfa-Aesar, UK) in dilute hydrochloric acid. The instrumental parameters were as follows: deposition potential  $-0.45$  V; deposition time up to 60 s (depending on sample concentration); voltage scan from  $-0.45$  to 0.1 V in DP mode at scan rate  $2 \text{ mVs}^{-1}$ ; pulse rate  $2 \text{ s}^{-1}$ ; pulse amplitude 20 mV; drop size  $0.52 \text{ mm}^2$ . The LOD of the method was  $11 \text{ ng L}^{-1}$  for a deposition time of 10 min, which amounts to  $2.75 \times 10^{-4} \mu\text{g g}^{-1}$  under the extraction conditions employed (i.e. 25 mL extractant for 1 g of solid sample). Electrolytes were degassed by sparging with 5N Ar (L'Air Liquide, Luxembourg).

In the presence of lactate, the voltammetric response was strongly depressed and somewhat erratic, possibly due to a complexation effect. This was corrected by the addition of a large excess of a trivalent cation: namely, 1 mL of a  $0.5 \text{ mol L}^{-1}$  solution of cerium (III)-chloride (heptahydrate p.a., Merck, Germany). The addition of  $\text{CeCl}_3$  did not alter the sensitivity of the voltammetric technique (slope of the linear calibration by standard addition) and spike-recovery experiments confirmed the applicability of the method in the presence of cerium ion. Whenever fresh extractant or  $\text{CeCl}_3$  solution had been prepared, blanks were determined and taken into account when found to be non-negligible. Blank values of the extractant itself were in general either below detection or of the order of  $10\text{--}100 \text{ ng L}^{-1}$ , while the addition of  $\text{CeCl}_3$  solution caused blank values to rise up to about  $0.5 \mu\text{g L}^{-1}$ . Procedural blanks (pure extractant solution carried through the whole protocol

without actual sample) showed that neither the PP centrifuge tubes and syringes nor the HDPE bottles used for reagent storage contributed to measurable concentrations of Sb. We conclude that blank signals were due to the p.a. quality of some reagents used for the preparation of the extractant or accidental contamination upon compounding.

### 2.8. Statistical treatment

Experiments were conducted in triplicate or quadruplicate. Dean and Dixon's Q-test failed to identify any outliers and therefore all experimental results were retained. Error margins presented reflect 95% confidence intervals and in order to assess statistical significance ( $\alpha = 0.05$ ), paired *t*-tests were used.

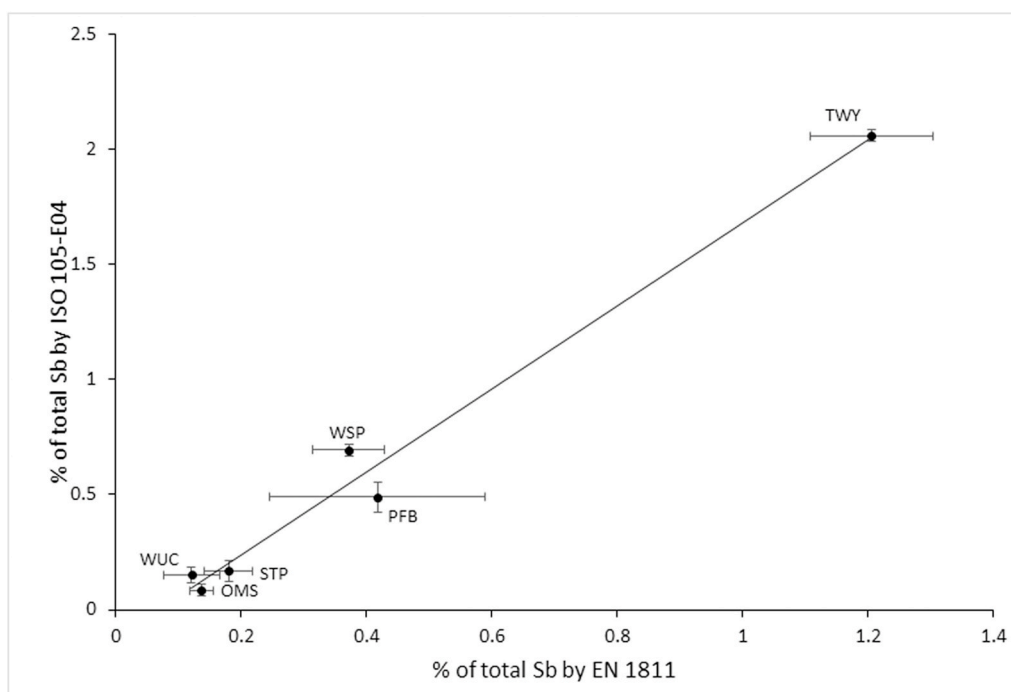
## 3. Results

Table 1 provides some general information on each sample. The SEM images illustrate the broad structure of each polyester textile and the nature and dimensions of individual fibres. Total antimony concentrations determined by XRF range from  $125 \mu\text{g g}^{-1}$  for a microfibre cloth (TWY) to  $471 \mu\text{g g}^{-1}$  for an old (used) shirt (OMS), and antimony extracted according to ISO 105-E04, with three 24-h sequential extractions at  $37^\circ\text{C}$ , ranged from  $0.402 \mu\text{g g}^{-1}$  for sample OMS to  $2.58 \mu\text{g g}^{-1}$  for sample TWY.

More detailed results of each individual extraction experiment are contained in Table S11. A possible explanation for negative extracted concentrations observed in some cases (typically occurring in the second fraction) may arise through re-adsorption of antimony from the remaining liquid of the preceding extraction onto the textile sample when the subsequent extractant fraction is added.

Extractions of the fleece blanket, PFB (PFB-1 to PFB-3), with ISO 105-E04 aimed to assess the repeatability of the protocol. Relative standard deviations of 6.3, 14.7 and 25.2% in antimony concentrations in the extraction stages 1, 2 and 3 were found at a total mobilization of  $0.904 \mu\text{g g}^{-1}$ . We deemed these deviations reasonable enough to consider the experimental approach as repeatable.

Fig. 1 shows the behaviour of ISO 105-E04 and EN 1811 when



**Fig. 3.** Relationship between the proportions of total extracted antimony by ISO 105-E04 and EN 1811. Linear regression results:  $y = 1.803x - 0.1223$ ;  $r^2 = 0.9830$ ,  $p$  (slope) = 0.00011,  $p$  (intercept) = 0.13. Error bars define 95% confidence interval.

applied to the six polyester textile samples following the standard protocol of three successive 24-h extractions at 37 °C and Fig. 2 shows the cumulative concentrations. In general, slightly more antimony is extracted by ISO 105-E04 than by EN 1811, which may be due to the higher pH of the latter (see below). The bulk of the extracted antimony can be found in the first fraction, with the extraction levelling off in fractions 2 and 3. Exceptions to this behaviour are found with EN 1811 applied to some samples (WSP, OMS and TWY) where the amount extracted remains constant or exhibits a small increase from fraction 1 to 3. OMS, the only sample of a used fabric, does not show a pronounced maximum in mobilization for the first step, likely because the readily mobile antimony has already been eliminated by many washing cycles over years of use. Nevertheless, and perhaps more importantly, it also reveals that used fabric continues to release antimony in small concentrations. An additional observation is that, with the exception of sample WSP, the extractable antimony pool appears to decrease with the total antimony concentration in the fibres as determined by XRF (Table 1).

Variations in the extraction protocol were probed by experiments using sample PFB and compared with the standard protocol (experiments PFB-1 to PFB-3) using the ISO 105-E04 solution. The results are summarized in Table 2 and described below.

Thus, a reduction of extraction time from 24 to 12 h (PFB-15, PFB-16, PFB-19) resulted in a significant decline (by about 15%) of the total mobilized antimony ( $0.770$  vs  $0.904 \mu\text{g g}^{-1}$ ) and lowering the extraction temperature to 20 °C (PFB-6, PFB-25, PFB-26, PFB-27) and to 4 °C (PFB-7, PFB-28, PFB-29) significantly reduced the extraction efficiency. The effect of varying the textile:extractant ratio from 1 g:25 mL (as suggested in Herrero et al., 2019) to 0.5 g:25 mL and 1.5 g:25 mL did not lead to significantly different extraction efficiencies.

The omission of the 0.1  $\mu\text{m}$  filtration step led to results higher by several percent, but the difference was never statistically significant (PFB-5, PFB-14, PFB-24, PFB-40, STP-2, STP-4, STP-5, TWY-1, TWY-2, TWY-4, TWY-5). This observation may be attributed to the formation of a variable number of small, loose fibres when samples were cut; this was particularly evident in sample TWY, a microfibre cleaning cloth that consisted of two layers of different fibres, one of which was only loosely interconnected (Figure S11). We hypothesize that if small fibres remain in the solutions to be analysed, this could lead to artificially high results because of prolonged dissolution of antimony during storage under acidification; fibre aspiration into an ICP plasma or AAS flame is also likely to result in magnified signals.

At pH 4 (PFB-8, PFB-35, PFB-36, PFB-42, PFB-43, PFB-44), the cumulated mobilization of antimony was almost identical to that at pH 5.5. However, mobilization decreased by 20% (albeit non-significantly;  $p = 0.0588$ ) when the pH was increased to 7 (PFB-9, PFB-45, PFB-46, PFB-47). More antimony was extracted in the presence of lactate (PFB-10, PFB-30, PFB-34), notably in the second extraction step, but the difference in cumulated extraction was not statistically significant. This is perhaps surprising as lactate, a component of human sweat, is known to form complexes with Sb(III) and Sb(V), as do all  $\alpha$ -hydroxycarboxylates at  $\text{pH} < 7$  (Tella and Pokrovski, 2009, 2012).

#### 4. Discussion

The insignificant effect of lactate on antimony release, together with the higher pH of the EN 1811 solution probably explains why less of the metalloid is mobilized by this solution than by ISO 105-E04 (Fig. 2), with the difference being statistically significant in two cases (Table 3). It should be noted, however, that sample OMS behaves atypically towards the extractants in that EN 1811 mobilizes more antimony than ISO 105-E04.

A plot of the proportion of total antimony extracted by ISO 105-E04 and the corresponding proportion extracted by EN 1811 shown in Fig. 3 reveals a significant linear relationship ( $r^2 = 0.9830$ ;  $p < 0.01$ ) with a gradient of 1.803 and intercept of  $-0.123$ . This suggests that, although both extractants target slightly different (but most probably

overlapping) pools of antimony, they do so in a repeatable way so that, in principle, both systems could serve as basis for a standardized test. We would, however, give preference to the ISO 105-E04 test, because this solution mobilized the bulk of the antimony in the very first extraction stage for most samples and its pH is closer to that of typical human sweat than EN 1811 (pH 5.3 is given as a median value of the pH of human sweat by Harvey et al. (2019); see also Schmidt-Wendtner and Korting (2006) for a comprehensive discussion of factors affecting the pH of human sweat). A further, practical, advantage of ISO 105-E04 is the absence of lactate such that the formulation is less prone to contamination by microbiological growth. A simplified standard procedure for the determination of mobile antimony in fabrics that affords meaningful results for both new and used fabrics could consist of a single extraction stage with ISO 105-E04, provided that the solution be filtered.

More generally, our study demonstrates that polyester textile fibres from fabrics meant to be in direct contact with human skin (blankets, pillowcases, swimwear, shirts) release antimony to sweat solutions in non-negligible amounts that are on the order of 0.1–1  $\mu\text{g Sb per g}$  of textile, corresponding to up to about 2% of the total antimony content of the material. Given the suspected toxicity of antimony, this is a problem that manufacturers and regulatory authorities should be aware of and address. Since the bulk of the mobilized antimony can be found in the first fraction of the simulated sweat solution, consumers can significantly minimize their risk of exposure by washing all synthetic textiles before their first use, preferably more than once; note that laundry is normally washed at a neutral to basic pH and at a temperature closer to 37 °C than the lower temperatures tested. The experiments with a sample of frequently worn and washed fabric (sample OMS) show that this does not, however, completely solve the problem as low concentrations of antimony continue to be released to sweat after multiple laundering cycles. On the basis of this study, one can also expect mobilization of antimony from polyester textile fibres to contribute to the global, diffuse pollution of the aquatic environment by the metalloid, both through the dissolution of antimony during laundering and the release of microplastic fibres into the environment.

#### 5. Conclusions

Although antimony is a ubiquitous catalytic residue in polyester fibres and may be present in a wider array of textiles as a flame retardant synergist, there is a dearth of information regarding its migration into human sweat and potential impacts through dermal exposure. Standard artificial sweat solutions (ISO 105-E04 and EN 1811) applied to a variety of polyester samples designed to be in contact with human skin have shown that up to 2% (or  $1 \mu\text{g g}^{-1}$ ) of total antimony is mobilized under default conditions, with a reduction occurring when time, temperature are decreased and pH is increased. ISO 105-E04 is recommended over EN 1811 for an assessment of antimony mobilization and exposure because its pH of 5.5 is closer to that of human sweat.

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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.

#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.yrtph.2020.104824>.



## References

- AATCC, 2013. TM015 Test Method for Colorfastness to Perspiration. American Association of Textile Chemists and Colorists.
- BSI, 2011. BS EN 1811:2011+A1:2015. Reference Test Method for Release of Nickel from All Post Assemblies Which Are Inserted into Pierced Parts of the Human Body and Articles Intended to Come into Direct and Prolonged Contact with the Skin. British Standards Institution.
- Bundesinstitut für Risikobewertung, 2012. Introduction to the problems surrounding garment textiles. Available at: [www.bfr.bund.de/en/health\\_assessment\\_of\\_textiles-531.html](http://www.bfr.bund.de/en/health_assessment_of_textiles-531.html) www.bfr.bund.de. Last accessed: November 2020.
- European Commission, 2014. Commission Decision of 5 June 2014 Establishing the Ecological Criteria for the Award of the EU Ecolabel for Textile Products (Notified under Document C(2014) 3677). Off. J. Eur. Union (L 174/45).
- Filella, M., 2020. Sb in PET: checking facts. *Chemosphere* 261, 127732.
- Harvey, C.J., LeBouf, R.F., Stefaniak, A.B., 2010. Formulation and stability of a novel artificial human sweat under conditions of storage and use. *Toxicol. Vitro* 24, 1790–1796.
- Herrero, M., Rovira, J., Nadal, M., Domingo, J.L., 2019. Risk assessment due to dermal exposure of trace elements and indigo dye in jeans: migration to artificial sweat. *Environ. Res.* 172, 310–318.
- ISO, 2013. ISO 105-E04. Textiles—Tests for Colour Fastness — Part E04: Colour Fastness to Perspiration, sixth ed. ISO, Geneva, Switzerland. 2013-03-15.
- Laursen, S.E., Hansen, O.C., Hansen, J., Pommer, K., Pedersen, E., Drøjdahl, A., Bernth, N., 2003. Survey of Chemical Compounds in Textile Fabrics, vol. 23. Danish Environmental Protection Agency - Danish Ministry of Environment and Energy.
- Licina, D., Morrison, G.C., Bekö, G., Weschler, C.J., Nazaroff, W.W., 2019. Clothing-mediated exposures to chemicals and particles. *Environ. Sci. Technol.* 53, 5559–5575.
- Matoso, E., Cadore, S., 2012. Determination of inorganic contaminants in polyamide textiles used for manufacturing sport T-shirts. *Talanta* 88, 491–501.
- Midander, K., Julander, A., Kettelarij, J., Lidén, C., 2016. Testing in artificial sweat – is less more? Comparison of metal release in two different artificial sweat solutions. *Regul. Toxicol. Pharmacol.* 81, 381–386.
- NTP, 2018. Report on Carcinogens. Monograph on Antimony Trioxide, Office of the Report on Carcinogens, National Toxicology Program. National Institutes of Health, Research Triangle Park, US.
- OEKO-TEX Association, 2018. Testing methods STANDARD 100 by OEKO-TEX®. Available at: [www.oeko-tex.com/importedmedia/downloadfiles/STANDARD\\_100\\_by\\_OEKOTEX\\_R\\_-\\_Testing\\_Methods\\_en.pdf](http://www.oeko-tex.com/importedmedia/downloadfiles/STANDARD_100_by_OEKOTEX_R_-_Testing_Methods_en.pdf). Last accessed: November 2020.
- OEKO-TEX Association, 2020. STANDARD 100 by OEKO-TEX®. Available at: [www.oeko-tex.com/importedmedia/downloadfiles/STANDARD\\_100\\_by\\_OEKO-TEX\\_R-ko.pdf](http://www.oeko-tex.com/importedmedia/downloadfiles/STANDARD_100_by_OEKO-TEX_R-ko.pdf). Last accessed: November 2020.
- Quentel, F., Filella, M., 2002. Determination of inorganic antimony species in seawater by differential pulse anodic stripping voltammetry: stability of the trivalent state. *Anal. Chim. Acta* 452, 237–244.
- Rovira, J., Nadal, M., Schuhmacher, M., Domingo, J.L., 2017. Trace elements in skin contact clothes and migration to artificial sweat: risk assessment of human dermal exposure. *Textil. Res. J.* 87, 726–738.
- Schmidt-Wendtner, M.-H., Korting, H.C., 2006. The pH of the skin surface and its impact on the barrier function. *Skin Pharmacol. Physiol.* 19, 296–302.
- Tella, M., Pokrovski, G.S., 2009. Antimony(III) complexing with O-bearing organic ligands in aqueous solution: an X-ray absorption fine structure spectroscopy and potentiometric study. *Geochem. Cosmochim. Acta* 73, 268–290.
- Tella, M., Pokrovski, G.S., 2012. Stability and structure of pentavalent antimony complexes with aqueous organic ligands. *Chem. Geol.* 292–293, 57–68.
- Textile Exchange, 2019. Textile-Exchange Preferred-Fiber-Material-Market-Report 2019. Available at: [https://store.textileexchange.org/wp-content/uploads/woocommerce\\_uploads/2019/11/Textile-Exchange-Preferred-Fiber-Material-Market-Report\\_2019](https://store.textileexchange.org/wp-content/uploads/woocommerce_uploads/2019/11/Textile-Exchange-Preferred-Fiber-Material-Market-Report_2019). Last accessed: November 2020.
- Turner, A., 2019. Trace elements in laundry dryer lint: a proxy for household contamination and discharges to waste water. *Sci. Total Environ.* 665, 568–573.