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Cadmium pigments in consumer products and their health risks

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Abstract

Cadmium is a toxic heavy metal that has been increasingly regulated over the past few decades. The main exposure routes for the general public are the consumption of certain foods and the inhalation of cigarette smoke. However, additional exposure may occur through the current and historical use of the metal in consumer products. In this paper, the uses of Cd in consumer goods are reviewed, with the focus on brightly-coloured Cd sulphide and sulphoselenide pigments, and measurements of Cd in historical and contemporary products ascertained by XRF are reported. Cadmium is encountered across a wide range of contemporary plastic products, mainly because of the unregulated recycling of electronic waste and polyvinyl chloride. However, concentrations are generally low ($<100 \mu\text{g g}^{-1}$), conforming with current limits and posing minimal risk to consumers. Of greater concern is high concentrations of pigmented Cd (up to 2% by weight) in old products, and in particular children's toys that remain in circulation. Here, tests conducted suggest that Cd migration in some products exceeds the Toy Safety Directive limit of $17 \mu\text{g g}^{-1}$ by an order of magnitude. The principal current use of Cd pigments is in ceramic products where the metal is encapsulated and overglazed. Leaching tests on new and secondhand items of hollowware indicate compliance with respect to the current Cd limit of $300 \mu\text{g L}^{-1}$, but that non-compliance could occur for items of earthenware or damaged articles should a proposed limit of $5 \mu\text{g L}^{-1}$ be introduced. The greatest consumer risk identified is the use of Cd pigments in the enamels of decorated drinking glasses. Thus, while décor is restricted to the exterior, any enamel within the lip area is subject to ready attack from acidic beverages because the pigments are neither encapsulated nor overglazed. Decorated glass bottles do not appear to represent a direct health hazard but have the propensity to contaminate recycled glass products. It is recommended that decorated glassware is better regulated and that old, brightly-coloured toys are treated cautiously.

Keywords: cadmium; plastics; ceramics; glassware; pigments; health

63

64 **1. Introduction**

65 Cadmium (Cd) is a cumulative toxin that is associated with kidney disease and that has effects on the
66 skeletal and respiratory systems (Larsson and Wolk, 2015). The heavy metal and its compounds are
67 also classified as known or probable, non-threshold human carcinogens by several regulatory
68 agencies, with data linking occupational exposure to lung cancer (Waalkes, 2003). Cadmium is widely
69 distributed in the environment at concentrations that are naturally low but that have increased
70 through human activities like smelting and refining of non-ferrous metals, fossil fuel combustion,
71 phosphate fertilizer manufacture, recycling of metal and electronic waste, and municipal waste
72 incineration (WHO, 2010). Because of its high rates of soil-plant and water-organism transfer, the
73 general population is exposed to Cd principally through inhalation of cigarette smoke and intake of
74 certain cereals, vegetables and seafoods (Satarug, 2012). Based on available epidemiological data,
75 the European Food Standards Authority has established a tolerable weekly intake of dietary Cd of 2.5
76 $\mu\text{g kg}^{-1}$ body weight (EFSA panel on contaminants in the food chain, 2011).

77 Cadmium as a metal, alloy or compound has had a variety of uses in consumer products, including
78 rechargeable batteries, items of jewellery and plastic goods, which pose an additional potential
79 source of human exposure, mainly through direct and indirect ingestion and in particular to children.
80 The risks are often difficult to quantify but based on our current and growing understanding of the
81 biological effects of Cd and its persistence in the human body, a precautionary principle is
82 recommended (Nawrot et al., 2010). Accordingly, various regulations and directives have been
83 introduced during the past three decades to protect consumers and the environment, examples of
84 which are defined in Table 1.

85 In this paper, the uses of cadmium and its compounds in products amenable to the consumer are
86 reviewed, with the focus on the occurrence of cadmium-based sulphide and sulphoselenide
87 pigments used to colour plastics, paints and ceramics, and where the metal is likely to appear in a
88 wide range of products where it is not necessarily expected or desired. New and published data
89 relating to the concentrations of Cd (and, for sulphoselenides, Se) in polymeric-based consumer
90 products or components thereof and gained through portable x-ray fluorescence (XRF) analysis by
91 the author's research group over the past few years are described and compared with values
92 defined by current and historical regulations. Data are also presented on the migration or extraction
93 of Cd from various products where regulations and standard tests are defined or implied.

94 **2. Uses of cadmium in consumer products and relevant regulations**

95 **2.1. Electronics**

96 In Cd-based sealed, rechargeable batteries, the metal serves as the cathode and NiOOH as the anode
97 in a potassium hydroxide electrolyte. The two electrodes and associated separators are rolled
98 together into a cylindrical configuration that is contained by a can, providing a nominal
99 electromotive force of 1.2 V. Although such cells have good life spans, and are reliable, versatile and
100 able to deliver their full capacity at high discharge rates, environmental concerns and newer,
101 superior alternatives have meant that the use of cadmium-based batteries has declined significantly
102 over the past two decades. Within the European Union, new Ni-Cd batteries are now only permitted
103 as replacements for specialist equipment (European Parliament and of the Council, 2006) that, as of
104 December 2016, excludes power tools (BIS, 2015a).

105 In electronics, Cd and its compounds are used as contacts for switches and relays, as colourants in
106 glass and filter glass and in printing inks applied to glass, as alloys in solder joints, in film pastes, and
107 in colour-converting light emitting diodes (BIS, 2011). The Restriction of the Use of Certain
108 Hazardous Substances in Electrical and Electronic Equipment (RoHS) Regulations have limited the
109 concentrations of Cd in any component or subassembly of new electrical and electronic equipment,
110 including plastic casings or insulation, to $100 \mu\text{g g}^{-1}$ (European Parliament and Council, 2003), while
111 the Institute of Electrical and Electronics Engineers Standard 1680 regarding personal computer
112 products states that Cd shall not exceed $50 \mu\text{g g}^{-1}$ in homogeneous materials unless demonstrably
113 present through recycle (IEEE, 2006).

114 **2.2. Jewellery**

115 Items of jewellery, and in particular cheap replicas that target children, have come under increasing
116 scrutiny over the past few years because of potentially high concentrations of alloyed Cd. For
117 instance, Weidenhamer et al. (2011) found Cd concentrations among several hundred charms,
118 pendants, bracelets and other embellishments sourced in the US that exceeded 10% by weight, with
119 quantities accessible to simulated saliva and dilute HCl that were highly variable but that exceeded
120 $2000 \mu\text{g}$ and $20,000 \mu\text{g}$, respectively, in some cases. Guney and Zagury (2014) found Cd
121 concentrations up to 37% by weight in various items of jewellery sourced in Canada with
122 bioaccessible concentrations of up to $165 \mu\text{g g}^{-1}$ derived from an in vitro gastrointestinal protocol. It
123 is suspected that more stringent controls on lead in consumer products, coupled with the
124 diminishing value of Cd as Ni-Cd batteries are phased out, has led to an increased production of Cd-
125 based jewellery in China for exportation (Olesen and Hoshiko, 2010). The EU has since prohibited the
126 use of Cd in metallic parts of jewellery, imitation jewellery and hair accessories according to

127 Regulation No. 494/2011 on cadmium (European Union, 2011), with a maximum permissible
128 concentration of $100 \mu\text{g g}^{-1}$ for items placed on the market after 2012.

129

130 **2.3. Polyvinyl chloride**

131 Cadmium was used in the form of a laurate or stearate as a stabiliser in polyvinyl chloride (PVC),
132 together with salts of barium and lead. Being heat-stable and resistant to ultra violet light, Cd-based
133 stabilisers were used extensively in outdoor plastics like window frames, doors and drainage
134 systems, but were also used for furniture, office equipment, apparel and clothing and wiring
135 insulation (European Chemicals Agency, 2013a). The European PVC industry began to voluntarily
136 phase out Cd-based stabilisers in 2001 before the EC prohibited their use in 2011 according to EU
137 Regulation 494/2011 (with the exception of recycled PVC in some construction plastics where Cd is
138 permitted at concentrations below $1000 \mu\text{g g}^{-1}$; European Union, 2011).

139 **2.4. Cadmium pigments**

140 As colourants, and because of their heat stability, chemical resistance, opacity, light fastness and
141 tinting strength, sulphides of Cd have been used extensively by the plastics and ceramics industries
142 (Wilson et al., 1982). Estimates suggest that the annual consumption of cadmium-based pigments
143 peaked at around 6000 tonnes in 1975, with the majority (~90%) used in plastics. Production has
144 been shrinking since because of both health and environmental concerns (European Chemicals
145 Agency, 2012), with information reported as of February 2018 indicating that current annual
146 production lies somewhere between 10 and 100 tonnes (Chemsec, 2018). Cadmium sulphide itself,
147 CdS, is a brilliant yellow (C.I. Pigment Yellow 37) but Zn (and sometimes Hg) as a cation and selenide
148 as an anion serve as exchangeable ions to effect different colour shadings. Specifically, cadmium zinc
149 sulphide, (Cd,Zn)S (C.I. Pigment Yellow 35), is a greenish yellow, and cadmium sulphoselenide,
150 Cd(S,Se), may be orange (C.I. Pigment Orange 20) or red (C.I. Pigment Red 108). These pigments are
151 produced by dissolution of Cd metal, with or without Zn, in mineral acid and subsequent
152 precipitation with sulphide or selenide; the filtered precipitate is then calcined in the absence of
153 oxygen at around 600-700 °C before being milled and blended (Pfaff, 2017).

154 Early risk assessments suggested that Cd sulphide pigments posed little risk to humans and the
155 environment because of their encapsulation by the polymeric matrix and extremely low solubilities
156 ($K_{\text{sp,CdS}} = 7.94 \times 10^{-27}$; $K_{\text{sp,CdSe}} = 6.31 \times 10^{-36}$) (Wilson et al., 1982; Kawasaki et al., 2004). However,
157 possible instability in the presence of acids, coupled with such widespread usage and potential
158 consumer exposure from a variety of sources, have resulted in calls for a re-evaluation of their

159 profiles (European Chemicals Agency, 2012). Significantly, recent research has highlighted the
160 environmental significance of the photosensitivities of CdS and CdSe pigments (band gaps of 2.5 and
161 1.8 eV, respectively), whose oxidised products (cadmium sulphate and cadmium selenite) are
162 considerably more soluble and bioavailable (Liu et al., 2017).

163 **2.4.1. Cadmium pigments in plastics**

164 Cadmium pigments were commonly employed to colour a variety of consumer plastics but were
165 particularly favourable where high processing temperatures and high-performance products
166 precluded the use of organic pigments (e.g. acrylonitrile butadiene styrene, polycarbonates and
167 high-density polyethylene; Wilson et al., 1982). Between 0.05 and 1.5% of Cd pigment by weight was
168 normally added to plastic as a powder and with a grain size in the range 1 to 3.5 μm . Being dispersed
169 in the matrix, the pigment exerts very little effect on the physical properties of the plastic, like
170 tensile strength and impact resistance (Scoullou et al., 2001).

171 Restrictions on the use of Cd pigments in plastics were introduced by individual nations in the 1980s
172 and currently the EU prohibits the use of Cd in most consumer products according to Regulation
173 494/2011 (European Union, 2011). Specifically, Cd concentrations are limited to 100 $\mu\text{g g}^{-1}$ in
174 products placed on the market after 2012, with the exception of articles coloured for safety reasons.
175 With the exception of recycled pallets and crates in closed loop schemes, Cd is also restricted to 100
176 $\mu\text{g g}^{-1}$ in plastics used for non-food packaging according to the European packing and packing waste
177 regulations (European Parliament and Council of the EU, 1994; BIS, 2015b). (Note that there have
178 been recent suggestions that Cd should be banned outright from all plastic products; European
179 Chemicals Agency, 2013a.)

180 Migratable Cd (in pigmented or any other form) is restricted in children's toys according to the
181 European Union Toy Safety Directive. The original Directive (88/378/EEC; Council of the European
182 Communities, 1988) stipulated limits for Cd and other toxic elements in a range of toys that could be
183 extracted by 0.07 M HCl at 37 °C according to the European Standard, EN 71-3 (BSI, 1995). The
184 maximum migratable concentration for Cd was set at 50 $\mu\text{g g}^{-1}$ but an amended Directive that
185 applied to products placed on the market from July 2013 provided revised limits for more specific
186 matrices, with the maximum concentration of Cd in "scraped-off" materials, including plastics, now
187 set at 17 $\mu\text{g g}^{-1}$ (European Parliament and Council of the EU, 2009).

188 **2.4.2. Cadmium pigments in ceramics and glassware**

189 With restrictions on the use of Cd compounds in plastics, their principal, remaining use has been as
190 decorative pigments for ceramicware and enamels for glass and porcelain products. Here, pigments

191 are partly dissolved into a matrix medium that adheres to the product. In ceramicware, the
192 decoration is glazed and fired at high temperature, in theory sealing any toxic compounds and
193 eliminating attack from food or washing solutions, while on glassware, the decorated product is fired
194 at a lower temperature. Cadmium sulphoselenides are one of only a few pigments that provide an
195 intense red colour but the compounds are not inherently stable at temperatures required for firing
196 ceramicware (750 to 1450 °C). This problem has been circumvented by encapsulating the pigments
197 in zircon, and mixing occluded sulphoselenides with other non-cadmium-based pigments is now able
198 to produce a wide range of colour shades (Lehman, 2002).

199 European regulations do not prohibit the use of Cd-based pigments for decorative purposes in food-
200 contact ceramicware, but relate to the concentrations of Cd extracted by dilute acetic acid according
201 to Directive 84/500/EEC (Council of the European Communities, 1984); the approach is effectively
202 the same as that defined by the ASTM for standard test C738-94 (ASTM, 2016). Thus, cleaned
203 articles are filled with test simulant, covered with opaque glass and left at $22 \pm 2^\circ\text{C}$ for 24 hours. For
204 shallow articles (flat-ware: internal depth < 25 mm), the limit for Cd release is $70 \mu\text{g dm}^{-2}$, while for
205 hollow-ware and cooking ware, limits are 300 and $100 \mu\text{g L}^{-1}$, respectively. However, evolving
206 knowledge about the accumulation and toxicity of Cd and World Health Organization drinking water
207 guidelines of just $3 \mu\text{g L}^{-1}$ (WHO, 2011) have resulted in calls for these limits to be lowered
208 significantly. Accordingly, a recent European Commission report has stipulated “discussing starting
209 values” of $1 \mu\text{g dm}^{-2}$ for flat-ware and $5 \mu\text{g L}^{-1}$ and $1.9 \mu\text{g L}^{-1}$ for hollow-ware and cooking ware,
210 respectively (Beldi et al., 2016).

211 California's Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65) has more
212 stringent guidelines on the Cd content of ceramics designed for food and beverages (Office of
213 Environmental Health Hazard Assessment, 2016). Thus, a prominently placed warning is required on
214 a product sold or distributed within the state if external decorations exceed limit values; specifically,
215 areas exclusive of the lip (within 20 mm of and including the rim) have a limit of $4800 \mu\text{g g}^{-1}$ total Cd
216 while the lip area itself has a limit of $800 \mu\text{g g}^{-1}$ Cd. A product may evade warning if it is shown to
217 release less than 7.92 mg L^{-1} Cd in dilute acetic acid according to a modified ASTM test only if it is not
218 designed for children.

219 Less clear and regulated are the quantities and migratabilities of Cd used in the coloured enamels on
220 glassware. Despite not being decorated internally, the risks of exposure may be greater on glass
221 articles because the pigments are over-glazed and subject to greater deterioration through abrasion
222 during use and storage and more readily exposed to chemical attack from foodstuffs and washing
223 solutions (Turner, 2018a). With respect to California's Proposition 65, the Cd content of decorated

224 glass articles appears to be subject to the same limits as ceramics ($4800 \mu\text{g g}^{-1}$ exclusive of the lip
225 area and $800 \mu\text{g g}^{-1}$ within this region) to trigger a prominent warning. Moreover, when tested with
226 C927 (ASTM, 2009), the internal volume-normalised concentration of Cd extracted by 4% acetic acid
227 from the 20 mm lip area must not exceed 4 mg L^{-1} (Calderwood and Bopp, 2005). There are no
228 equivalent guidelines provided by the EU, and Poland appears to be the only member state to have
229 its own regulations that stipulate a 0.2 mg limit for Cd extractable from the lip area in dilute acetic
230 acid (Rebeniak et al., 2014).

231 **2.4.3. Cadmium pigments in paints**

232 Because of their brilliant shades, Cd sulphide-based paints have been popular with artists since the
233 mid-19th century. The Cd content of contemporary artists' paints ranges from 12.1 % in acrylics to
234 about 35 % in oil and water-based paints, with the latter having the largest market share (European
235 Chemicals Agency, 2015). In Europe, around 40 tonnes of artists' paints are sold annually, which is
236 equivalent to over 6000 kg of Cd (Bandow and Simon, 2016).

237 Cadmium is restricted in consumer paints sold in the European Union to concentrations of $100 \mu\text{g g}^{-1}$
238 unless the Zn content exceeds 10% (Cd is then restricted to a concentration of $1000 \mu\text{g g}^{-1}$)
239 (European Union, 2016). However, unlike plastics, Cd sulphide-based pigments are currently not
240 regulated in artists' paints or the pigments used to directly prepare them. In December 2013, the
241 Swedish Chemicals Agency, KEMI, submitted a proposal to the European Chemicals Agency calling
242 for Cd-based pigments to be restricted in artists' paints on the basis that excess material washed
243 into sewers could contaminate agricultural land through the application of sewage sludge as a
244 fertiliser (European Chemicals Agency, 2013b). However, the ECHA concluded that the risk of
245 exposure was minor and that the input of Cd to the environment through this source was very small
246 compared with inputs from other sources (European Chemicals Agency, 2015). Subsequent
247 percolation experiments performed using soil amended with sludge and spiked with Cd pigments
248 also confirmed that the solubility of pigment-bound Cd was low and that Cd pigments did not lead to
249 an increase in leachable or bioavailable Cd in soil (Bandow and Simon, 2016).

250 The human exposure to Cd evaluated above is indirect (via the contamination of wastewater,
251 sewage sludge, agricultural soil and crops) and is averaged for the general population. However, Cd
252 exposure restrictions listed in Table 1 largely relate to or imply direct exposure to the consumer
253 through handling of a product (e.g., toys, jewellery, ceramics, decorated glassware) and ingestion of
254 the metal. Thus, although artists' paints constitute a small (but growing) proportion of Cd pigment
255 use, artists themselves are subject to more direct risk of exposure through preparing and handling
256 materials and contaminating hands, clothing and food. The bioaccessibility of Cd in paints via

257 ingestion does not appear to have been studied directly but it would be reasonable to predict
258 greater solubility in the more acidic environment of the human stomach than that of rainwater used
259 to simulate leaching from agricultural soils. Specifically, speciation calculations performed by
260 Bandow and Simon (2016) demonstrate that the solubility of CdS increases exponentially with
261 decreasing pH such that well over 10% of Cd could be mobilised under the conditions typical of the
262 stomach. Thus, for an artists' paint containing 35% Cd whose bioaccessibility is 10%, ingestion of
263 only 5 to 6 mg of paint could be equivalent to the weekly tolerable intake of Cd of an adult of 50 to
264 60 kg ($2.5 \mu\text{g kg}^{-1}$; EFSA panel on contaminants in the food chain, 2011).

265

266 **3. Measurement of cadmium and cadmium migration in consumer products**

267 Cadmium and other elements may be determined rapidly and non-destructively in consumer
268 products, including plastics, ceramics, paints and enamels, by portable x-ray fluorescence (XRF)
269 spectrometry. To this end, the author has analysed an extensive number of samples as part of
270 research into antimony and bromine in household plastics (Turner and Filella, 2017a; 2017b),
271 hazardous elements in children's toys (Turner, 2018b), and metals in decorated glass enamels
272 (Turner, 2018a). Here, data for Cd (and Se) in these samples are synthesised, and additional samples,
273 including household ceramics and beverage bottles, have been analysed for the specific purposes of
274 the current paper.

275 Briefly, a broad range of commonly used plastic, glass and ceramic consumer products were
276 borrowed from or supplied by various local households, offices, nurseries and schools, or were
277 purchased new or second-hand from different retail outlets (including hardware stores, gift shops,
278 supermarkets and charity shops). Samples (whole products or distinctive components or regions
279 thereof, like different parts of a toy, puzzle, tool or appliance, or different coloured areas of ceramics
280 or enamelled glass) were analysed using a Niton XLT3 He GOLDD+ portable XRF that was deployed in
281 situ and with appropriate shielding or in the laboratory and nose-upwards in a tungsten-lined
282 accessory stand. Counting was performed in a standard-less plastics mode for 30 s to 1 min,
283 comprising periods equally distributed between two different energy ranges (40 μA and 50 KVp, and
284 100 μA and 20 KVp). For plastics, a thickness correction was applied after the thickness of the
285 measurement area was measured or estimated, while for ceramics and for enamels on glassware
286 and painted surfaces, respective thicknesses of 0.1 mm or 0.05 mm were assumed. For quality
287 assurance purposes, two polyethylene reference discs (PN 180-619, LOT#T-18, Cd = $292 \pm 20 \mu\text{g g}^{-1}$
288 and Se = $207 \pm 15 \mu\text{g g}^{-1}$; PN 180-554, batch SN PE-071-N, Cd = $150 \pm 6 \mu\text{g g}^{-1}$) were analysed at
289 regular intervals throughout each measurement session. Data, as spectra and concentrations in $\mu\text{g g}^{-1}$

290 $1 \pm 2\sigma$, were downloaded to a laptop using Niton data transfer software. Detection limits under
291 these conditions (as 3σ) varied inversely with sample thickness and ranged from about 15 to 150 μg
292 g^{-1} for Cd in plastics and from about 150 to 400 $\mu\text{g g}^{-1}$ for Cd in ceramics, paints and enamels;
293 detection limits for Se were more variable, with respective ranges of about 12 to 250 $\mu\text{g g}^{-1}$ and 50
294 to 500 $\mu\text{g g}^{-1}$.

295 The migration of Cd was determined in selected products according to appropriate methodologies.
296 Specifically, various colourful components of old toys, games and puzzles were extracted in 0.07 M
297 HCl according to EN 71-3 (BSI, 1995), while ceramics and decorated glassware were extracted in
298 acetic acid according to Directive 84/500/EEC (Council of the European Communities, 1984) and
299 various, but standardised, modifications. Extracts arising from these tests were analysed by
300 inductively coupled plasma-mass spectrometry or inductively coupled plasma-optical emission
301 spectrometry under operating conditions defined elsewhere (Turner, 2018b).

302

303 **4. Cadmium concentrations in consumer products**

304 **4.1. Plastics**

305 Results arising from the analysis of about 1500 consumer plastic products or components thereof,
306 roughly equally divided among six sample categories, are summarised in Table 2. Overall, Cd was
307 detected in 111 cases, or in about 7% of all samples tested. In the food-contact category, Cd was
308 positive in several black items of food packaging, various components of coffee jugs or presses, a
309 thermos flask lid and a clear plastic drinks bottle, none of which were of PVC construction. Although
310 mean and median concentrations were the lowest among the six categories considered, in three
311 cases concentrations exceeded 100 $\mu\text{g g}^{-1}$ and would, therefore, be non-compliant according to
312 various regulations or directives (Table 1). In the construction-storage category, Cd was detected
313 across a wider range of colours and at more variable concentrations. Concentrations below 100 $\mu\text{g g}^{-1}$
314 were largely restricted to black products, including a shampoo bottle cap, a clothes hanger and a
315 castor, with the highest concentrations encountered in white PVC door and window frames and in
316 brightly coloured items that included an orange ballcock float. Regarding the clothing-accessory
317 category, Cd was only detected in items of (mainly black) non-PVC-based plastic jewellery, including
318 beads, a pendant, an earring and, at 35,000 $\mu\text{g g}^{-1}$, a brooch.

319 Cadmium was most frequently detected in the toys-hobbies category and across a wide range of
320 products and colours. Here, PVC products that contained detectable Cd (and at concentrations
321 ranging from 38 to 770 $\mu\text{g g}^{-1}$) included the black wheels and tracks of several toy vehicles, orange

322 and red rubber ducks, and a number of model dinosaurs of various colours. Concentrations of Cd
323 above 1000 $\mu\text{g g}^{-1}$ were, however, restricted to an abundance of old, brightly coloured (and mainly
324 yellow or red) non-PVC-based components of toys, games and puzzles. In the office-garden category,
325 Cd was most commonly encountered in black tool handles, but concentrations above a few hundred
326 $\mu\text{g g}^{-1}$ were found in a black PVC tool wallet, the black body of a strapped document carrier and the
327 black frame of a chair, with the highest concentration (13,400 $\mu\text{g g}^{-1}$) returned for the red handle of
328 a staple gun. Cadmium concentrations in the electronic and electrical equipment (EEE) category
329 spanned two orders of magnitude and the metal was present in mainly black, grey and white plastic
330 casings and insulating material, of which one sample (a white wire insulator) was PVC-based.

331 There is clear evidence of the direct, albeit historic, use of Cd as a stabiliser in PVC products designed
332 for external exposure (door and window frames) and at concentrations up to about 1 % by weight.
333 However, the presence of Cd at much lower concentrations in a range of PVC products (but mainly
334 components of toys) suggests that historical PVC may have been recycled and blended into more
335 contemporary consumer goods. Regarding non-PVC-based products, the presence of Cd at
336 concentrations below 100 $\mu\text{g g}^{-1}$ may be attributed to the presence of traces of PVC as a contaminant
337 in other plastics. Alternatively, Cd may be present in new consumer products through the prohibited
338 (but often unregulated) recycling of waste EEE plastic, where the metal is encountered as a
339 contaminant through its various uses in electrical components and its concentration is restricted
340 (Table 1). This process is a particular problem for black plastics because of the technological
341 difficulties in sorting materials of this colour in the conventional domestic waste stream (Turner,
342 2018c). Consistent with this assertion, there was a prevalence of small quantities of Cd among black,
343 non-PVC-based samples, as indicated earlier and that included items of jewellery, tool handles,
344 components of toys, bottle tops, clothes hangers and coffee presses.

345 Also shown in Table 2 are cases in which Cd was suspected as being present in the form of a sulphide
346 or sulphoselenide pigment. Here, articles were distinctively coloured (mainly red-orange-yellow, but
347 occasionally pink or brown) and non-PVC-based, and contained relatively high concentrations of Cd
348 and, often, Se. Overall, 24 coloured samples (or about 10 % of those analysed, and none of them
349 purchased new) appeared to be pigmented by Cd, with the majority of products components of old
350 children's toys that remain in circulation. The concentrations of Cd and Se in these samples are
351 shown in Table 3, along with the principal colours and, where known, product name, manufacturer
352 and approximate date of original sale; a selection of toys returning the highest concentrations of Cd
353 is also illustrated in Figure 1. Concentrations of the metal span two orders of magnitude, with a
354 range that is consistent with that reported for Cd-pigmented plastics more generally (Scoullos et al.,
355 2001), and the highest concentrations occur in red and yellow ABS bricks and other components

356 from various Lego sets that appear to have been purchased new in the 1970s. Selenium was only
357 detected in red and orange samples where Cd concentrations exceeded $1500 \mu\text{g g}^{-1}$, and the best fit
358 line of [Cd] versus [Se] forced through the origin ($n = 8$, $r^2 = 0.963$; Figure 2) revealed an average
359 mass ratio of [Cd]:[Se] of about 6.4.

360 **4.2. Ceramics**

361 A total of 174 XRF measurements were performed on 75 glazed ceramic products purchased in the
362 UK that included mugs, plates, bowls, teapots, jars, egg cups, jugs and items of cutlery of either a
363 single colour or of multiple colours that constituted a repeating pattern, image or motif.
364 Measurements targeted regions of different colour on the same surface or different surfaces or
365 components of the same product (such as the handle, rim, base and interior). Summary statistics for
366 the ceramic analyses, shown in Table 4, indicate that Cd was detected as a sulphide or
367 sulphoselenide pigment in 87 cases (or in more than 50 % of analyses performed), often under a
368 lead-based glaze, and across all types of product that were sourced both new and second-hand and,
369 where indicated, were manufactured in both Europe and east Asia. The metal was present in
370 coloured areas that were red, orange, yellow, brown, pink, purple and green but not white, black or
371 blue. Selenium was detected with Cd in 59 cases in which the colour was either red or orange, and
372 the best fit line of [Cd] versus [Se] forced through the origin ($r^2 = 0.751$; Figure 2) indicated an
373 average mass ratio of [Cd]:[Se] of 8.0 and slightly higher than the corresponding ratio for pigmented
374 plastics (see above).

375 Overall, measured Cd concentrations ranged from about 50 to $40,000 \mu\text{g g}^{-1}$, with concentrations
376 below $1000 \mu\text{g g}^{-1}$ usually associated with yellows and greens and concentrations above $5000 \mu\text{g g}^{-1}$
377 always returned by shades of red. Significantly, 14 items of hollow-ware (mainly drinking mugs),
378 most of which were purchased new, contained detectable Cd in the lip area (including the rim)
379 and/or the interior, with concentrations ranging from about 200 to $40,000 \mu\text{g g}^{-1}$; other items where
380 Cd was detected in regions that would be in direct contact with food included two plates, a ladle, a
381 tea spoon and a storage jar. Regarding California's Proposition 65, a total of 28 products, all of which
382 were drinking mugs, would potentially require a warning label based on a Cd content exceeding
383 $4800 \mu\text{g g}^{-1}$ used in the decorative paint and/or a Cd content exceeding $800 \mu\text{g g}^{-1}$ in the lip area.
384 (Note that, strictly, limit values on total Cd are based on nitric acid-hydrogen peroxide digestion but
385 for the purposes of the present discussion, non-destructive XRF measurements are assumed to be
386 equivalent.)

387 **4.3. Decorated glassware**

388 The presence and concentrations of Cd in enamelled decorations on drinking glasses (including
389 tumblers, jars, highballs, beer glasses, wine glasses and shot glasses) have been reported in an
390 earlier publication (Turner, 2018a) and are summarised in Table 4 and below. Briefly, Cd was
391 detected in about 70 % of the 197 logos, patterns, text, pictures and cartoons tested on 72 products.
392 Cadmium was often present in association with a lead-based glaze and was detected on both new
393 and second-hand products that had been manufactured in Europe, Turkey and China.
394 Concentrations ranged from a few hundred $\mu\text{g g}^{-1}$ to about 70,000 $\mu\text{g g}^{-1}$ and although levels were
395 higher than in ceramic products according to any statistical descriptor, decorations were restricted
396 to the exterior of the product and covered a smaller area (typically between 5 and 50% of the
397 external surface). Although the highest concentrations and greatest occurrence of Cd was in red and
398 orange enamels, the metal was detected across a wide range of colours tested that included blue,
399 white and black. It was suspected, therefore, that Cd had additionally been employed as a
400 component of the flux (e.g. as CdO) (Demont et al., 2012). Selenium was also present across a wider
401 range of colours but restricting measurements to shades of red and orange (and minimising
402 interferences from any components of the flux) the average mass ratio of [Cd]:[Se] was about 10.2
403 based on the best fit line of [Cd] versus [Se] forced through the origin ($n = 38$, $r^2 = 0.921$; Figure 2).
404 According to California's Proposition 65, 42 of the tested products, including many targeting
405 children, would potentially require a warning label based on either or both an exceedance of 4800
406 $\mu\text{g g}^{-1}$ Cd in any enamelling and an exceedance of 800 $\mu\text{g g}^{-1}$ Cd in enamel encroaching into the lip
407 area.

408 Bottles for alcoholic drinks (e.g. wines, beers, liqueurs, spirits) are frequently externally embossed
409 with enamelled decorations and logos and yet do not appear to have received any attention in
410 respect of the use of heavy metals in the scientific literature. Mention is made of Cd pigments in
411 brightly-coloured enamels on glass bottles in the European packaging and packaging waste
412 regulations (European Parliament and Council of the EU, 1994), although it is claimed that many
413 major producers have signed a voluntary agreement aiming to phase out use of the metal (BIS,
414 2015b). In the present study, 18 decorated bottles purchased from national supermarkets were
415 subject to XRF analysis, once the contents had been consumed. The results, summarised in Table 4,
416 reveal that Cd was detected in 11 out of 36 analyses performed that encompassed various colours
417 on seven individual products; namely, four bottles of wine, a bottle of cider, a bottle of beer and a
418 bottle of advocaat, whose origins were noted as being Australia (x 2), South Africa, Spain, Chile, the
419 UK and the Netherlands (a selection of which is illustrated in Figure 3). On the wine bottles, Cd was
420 always associated with Pb, presumably as a component of the flux, and where Cd was present in red

421 enamelled text or decoration, Se was detected; the mean mass ratio of [Cd]:[Se] was about 12 based
422 on the best fit line of [Cd] versus [Se] forced through the origin ($n = 4$, $r^2 = 0.947$; Figure 2).

423 **4.4. Paints**

424 Two water-mixable oil-based artists' paints (artisan cadmium red light and artisan cadmium red
425 dark; Windsor and Newton) that had been purchased from a national hardware store were analysed
426 as part of this study. The presence of Cd was not explicitly referred to on the product labels but
427 mention was made in small print that the paints contained a substance known to be carcinogenic by
428 the state of California. Paints were applied to glass slides with a brush and allowed to air-dry in a
429 fume cupboard for 48 hours before being measured by portable XRF as films of thickness 0.05 mm.
430 Cadmium concentrations of over 500,000 $\mu\text{g g}^{-1}$ were returned for both paints, with accompanying
431 concentrations of Se exceeding 50,000 $\mu\text{g g}^{-1}$. Concentrations of Cd are greater than the range
432 reported for paints by the European Chemicals Agency (2015) and should be regarded as indicative
433 because it is unlikely that the XRF is calibrated for such high quantities of the metal. Nevertheless,
434 the mass ratios of [Cd]:[Se] of about 10.5 are consistent with those reported for other products
435 pigmented by Cd and as illustrated in Figure 2.

436 Although such paints are designed for artists, consumers may encounter Cd-based paints of various
437 colours on oil-, acrylic or water-based paintings that have been purchased or commissioned. As an
438 example, a brightly-coloured oil painting acquired by the author revealed Cd concentrations of about
439 40,000 $\mu\text{g g}^{-1}$ in areas painted orange while other colours (purple, pink, green and yellow) appeared
440 to be Cd-free. Cadmium was also present at concentrations up to 5000 $\mu\text{g g}^{-1}$ in the red, decorated
441 areas of glazed products that had been cast and subsequently painted by customers, including
442 children, at commercial ceramic and pottery studios. This affords a more direct, albeit occasional,
443 exposure route of pigmented Cd paints for members of the public.

444 A recent, independent study has also revealed that exposure to Cd paint may be significant through
445 painted wooden and steel chopsticks (Zhao et al., 2018). Here, Cd concentrations determined by
446 atomic absorption spectrometry following acid digestion were reported to be as high as 118,000 μg
447 g^{-1} in the decorated support regions of samples purchased on the east Asian market but that may be
448 representative of chopsticks exported farther afield.

449

450 **5. Accessibility of Cd in consumer products**

451 Although the concentrations of Cd reported above for plastics, ceramics, enamels and paints may be
452 cause for concern, critical to the health impacts of the metal is its accessibility in or migratability

453 from the matrix. Specifically, since ingestion and, for young children, mouthing, are likely to be the
454 principal means of exposure, Cd solubility in digestive fluids or in food will be a key factor in any risk
455 assessment.

456 **5.1. Plastics**

457 For non-food contact articles, and in particular children's plastic toys pigmented with Cd, it was
458 assumed by manufacturers that health risks were minimal because the fine sulphide or
459 sulphoselenide particulates are protected by an insoluble layer of plastic. However, a British
460 Standards report mentioned by Fowles (1977) suggested that 1% of Cd could leach from acrylonitrile
461 butadiene styrene (ABS) under simulated acidic stomach conditions. To this end, Fowles (1977)
462 himself investigated more systematically the factors controlling the leaching of Cd from ABS that had
463 been impregnated with red CdSe or yellow CdS. Leaching was found to be dependent on the
464 strength of HCl employed, shaking speed, temperature, the presence of air, and particle size and the
465 means of particle grinding; however, the most important factor in the experiments was the presence
466 or absence of light, compared under a 500 W photoflood lamp and in a series of darkened, foil-
467 wrapped bottles. Thus, under otherwise identical conditions (1 g of 0.1 to 0.5 mm particles in 25 ml
468 0.1 M HCl for 4 h at 37.5 °C), the quantities of Cd released from red ABS in light and dark were an
469 order of magnitude different (180 µg and 16 µg, respectively); Cd release from yellow ABS was less
470 sensitive to light, but differences were still clear (112 µg and 45 µg in light and dark, respectively).
471 These observations may be attributed to the photosensitivity of both Cd compounds, and indicate
472 that any meaningful studies on (pigmented) Cd bioaccessibility from plastics must be performed
473 under the exclusion of light. Such empirical studies have formed the basis of the European Union Toy
474 Safety Directive, as outlined above and defined in Table 1.

475 A recent investigation into the migratability of toxic elements from children's plastic toys revealed
476 that many individual items (components of games or sets) were non-compliant with respect to both
477 the original and recast Toy Safety Directives (Turner, 2018b). Concentrations of migratable Cd, based
478 on data presented in Turner (2018b) and on new measurements performed as part of the current
479 study, are shown for the individual samples, where tested, in Table 3. These measurements reveal
480 non-compliance for the ABS Lego pieces, with a maximum migratable concentration of over 200 µg
481 g⁻¹, or just over 1 % of total Cd as determined by XRF; inadvertent consumption of 100 mg of this
482 material by a child of 8 kg would be equivalent to its tolerable weekly intake for the metal. On a
483 percentage migration basis, the range of results for Lego are comparable to the range derived by
484 Fowles (1977) for unspecified red and yellow ABS. However, it is conceivable that higher absolute

485 concentrations reported in Table 3 may have arisen through aging and partial photo-oxidation of the
486 pigmented particulates.

487 **5.2. Ceramics**

488 The leaching of Cd from ceramic tableware and cooking ware has been closely monitored in many
489 countries since the early 1970s (Mourareau, 1978), with harmonisation of various different practical
490 approaches resulting in internationally-recognised tests based on extraction in cold, dilute acetic
491 acid. As with the Toy Safety standard, a critical condition of the test, which is not always stipulated
492 clearly and may explain large discrepancies observed in inter-laboratory trials, is that extraction be
493 performed in the dark due to the photosensitivity of Cd sulphides and sulphoselenide pigments. The
494 release of Cd proceeds via two successive reactions (Halpin et al., 1978): thus, firstly, Cd and other
495 constituents are released from the glaze by acid attack, with some potential release from the
496 underlying crystalline (pigmented) phase; secondly, the crystalline phase is attacked by the acid in a
497 photosensitive reaction. In practice, therefore, Cd extraction will be dependent on factors like
498 storage time, the acidity and opacity of food or drink, and the presence of any oxidants or
499 antioxidants.

500 Selected samples ($n = 10$) that were Cd-positive on the interior surface (or part thereof) as
501 determined by XRF and that were non-compliant with respect to California's Proposition 65 total Cd
502 limits were extracted according to Directive 84/500/EEC and the results are shown in Table 5. Note
503 that all products satisfying these criteria were items of hollow-ware, and that five products had been
504 used prior to testing. Concentrations of extractable Cd range from $< 0.1 \mu\text{g L}^{-1}$ to about $15 \mu\text{g L}^{-1}$ and
505 do not appear to be related to the concentration of total Cd. There is no evidence of elevated
506 concentrations arising from prior usage, but damage to the interior glazing (specifically, a vertical
507 hairline crack) and relatively low firing temperature (for earthenware) appear to accentuate Cd
508 migration. Cadmium concentrations for all items tested were well below the current $300 \mu\text{g L}^{-1}$
509 European limit, but the damaged and earthenware products would be non-compliant according to
510 the new, proposed limit of $5 \mu\text{g L}^{-1}$ (Beldí et al., 2016).

511 **5.3. Decorated drinking glasses**

512 Results arising from the acetic acid extraction of the 20 mm lip area of drinking glasses are given in
513 Turner (2018a) and summarised as follows. Thus, 16 new and second-hand products were tested for
514 extractable Cd, with interior volume-normalised concentrations ranging from $< 10 \mu\text{g L}^{-1}$ to around
515 $40,000 \mu\text{g L}^{-1}$ and five items non-compliant according to California's Proposition 65; significantly,
516 concentrations up to about $3000 \mu\text{g L}^{-1}$ were released by a popular soft drink (Coca Cola Classic).

517 Overall, acetic-extractable concentrations were orders of magnitude greater than concentrations
518 released by the acid from ceramic hollow-ware products under equivalent conditions, and for one
519 product (a mug decorated with repeating red rings, illustrated in Figure 3), a single acetic acid test
520 mobilised 40 times the weekly tolerable intake for an adult of 50 kg. Presumably the high mobility of
521 the metal is due to Cd pigments being incorporated into the frit that is fired and over-glazed at a
522 lower temperature on glassware and, potentially, because there is little (or no) requirement for
523 pigment particle encapsulation by zircon. The latter assertion was explored by comparing spectra of
524 Cd-positive ceramic articles and Cd-enamelled drinking glasses, and as exemplified in Figure 4; thus,
525 in nearly all ceramic products, a distinct zirconium peak ($Zr_{K\alpha}$) was observed at 15.78 keV that was
526 absent on enamelled glass. Release of crystalline Cd from decorated glassware is not, therefore,
527 constrained by the erosion of the glaze or zirconium silicate but proceeds directly through acidic
528 attack of the enamel.

529 Presumably, decorations on glass beverage bottles are subject to the same process of acid attack,
530 given that the décor is not over-glazed and the pigments are not encapsulated by zircon (and as
531 confirmed by examination of XRF spectra). While the handling of decorated bottles is likely to pose
532 minimal risk of Cd exposure to the consumer, the recycling of such products is a potential source of
533 Cd contamination of the raw cullet and new glassware.

534

535 **6. Discussion and concluding remarks**

536 This study has illustrated the type of contemporary and historical (non-metallic) consumer goods in
537 which Cd is present, with the focus on Cd in the form of pigmented sulphides and sulphoselenides.
538 Small quantities of Cd appear to be heterogeneously dispersed among consumer plastics, an effect
539 that may be attributed to the recycling and blending of electronic waste and PVC. While typical
540 concentrations reported are within the most recent regulatory limits and are unlikely to pose a
541 significant risk to consumers, the widespread occurrence of the metal highlights the poor and
542 inefficient practices involved in sorting and managing end-of-life products, and in particular plastic
543 housings of electronic equipment (Turner, 2018c).

544 Pigmented Cd was never detected in new plastic goods in the present study. By comparison, analysis
545 of beached plastic litter from south west England reveals a frequent occurrence of brightly coloured
546 (mainly red, orange and yellow) Cd-containing samples including bottle tops, gun cartridges and
547 ropes as well as unidentifiable fragments of varying sizes and shapes (Turner, 2016; Massos and
548 Turner, 2017). This observation is consistent with the incorporation of Cd pigments in single-use

549 items and consumer plastics that are no longer in circulation (Hansen et al., 2014). Plastics in which
550 Cd is most likely to be encountered by the contemporary consumer are brightly coloured
551 components of popular old toys, games and puzzles that have been re-sold or handed down. Here,
552 total Cd concentrations can be as high as 2% by weight and migratable concentrations may exceed
553 the current toy safety limit of $17 \mu\text{g g}^{-1}$ by more than an order of magnitude. Of most concern in this
554 respect are small, mouthable products or components that are designed for young children and that
555 are visibly worn or damaged.

556 With restrictions on the use of Cd in plastics, the principal current use of pigmented Cd is in
557 decorated ceramic products. Although total interior concentrations of the metal on articles designed
558 for food and drink may exceed levels that trigger a California Proposition 65 warning about potential
559 health impacts, standard tests conducted on new products purchased in the UK (but manufactured
560 in various countries and regions) as part of the study indicate that migratable concentrations are
561 well below the current European limit of $300 \mu\text{g L}^{-1}$. A proposed, significant downward revision of
562 this figure to $5 \mu\text{g L}^{-1}$, however, will prove more challenging for manufacturers, and especially for
563 those producing earthenware that is fired at relatively low temperatures. The revised limit may also
564 be exceeded more generally should goods become damaged or worn and it is recommended that
565 clear advice is given to consumers about the condition of ceramic items used to store or serve food
566 and drinks. It should also be borne in mind that Cd usually co-exists with other toxic metals in
567 ceramic products (and mainly lead in the glaze) and that there are uncertainties about the suitability
568 of the present testing protocol. With respect to the latter, conducting extractions in the dark when
569 Cd pigments are known to be photosensitive is bound to underestimate Cd migration and appears to
570 contradict the precautionary approach that is generally advocated (Nawrot et al., 2010).

571 Despite more limited décor that is restricted to the exterior surfaces, enamelled drinking glasses
572 pose a greater risk of Cd exposure to consumers, and in particular to children. This is because Cd
573 pigments fused to glass are considerably more accessible than when sealed on ceramics by glazing.
574 Thus, without zircon encapsulation and a protective layer of glazing, Cd is subject to direct attack in
575 the painted lip area if an acidic drink is being consumed. Although empirical studies have shown
576 that, for some products, distinct discolouration and even deterioration of the décor may occur
577 (Turner, 2018a), in many cases, and to the consumer, Cd may be mobilised without any obvious
578 visible modification of the enamelled surface. Many bottles used for the storage of drinks are also
579 enamelled with Cd-based pigments and, while not posing a significant risk to consumers, have the
580 potential to contaminate recycled glass products.

581 Given the potential health risks associated with externally decorated glass hollow-ware, and
582 especially for articles that target children, it is recommended that further studies focus on the
583 physical and chemical makeup of contemporary enamels and the release of heavy metals therefrom,
584 and that suitable standardised regulations are devised and enforced.

585

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589

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Table 1: Regulations relevant to the use of cadmium in consumer goods.

Regulation/Directive	Product type	Permissible Cd	Reference
Directive 2006/66/EC	Batteries and accumulators	New Ni-Cd batteries only permitted in certain applications	European Parliament and of the Council (2006)
Directive 2002/95/EC	Electrical and electronic equipment	< 100 $\mu\text{g g}^{-1}$ in any (plastic) component of new equipment	European Parliament and Council (2003)
IEEE Standard 1680	Personal computers	< 50 $\mu\text{g g}^{-1}$ in any homogenous material	IEEE (2006)
Regulation 494/2011	Jewellery	< 100 $\mu\text{g g}^{-1}$ for new products	European Union (2011)
	Plastic consumer products	< 100 $\mu\text{g g}^{-1}$ for new products ^a	
Directive 88/378/EEC	Toys	< 50 $\mu\text{g g}^{-1}$ migratable Cd	Council of the European Communities (1988)
Directive 2009/48/EC	Plastic toys	< 23 $\mu\text{g g}^{-1}$ (now < 17 $\mu\text{g g}^{-1}$) migratable Cd	European Parliament and Council of the EU (2009)
Children's Jewellery Regulations	Jewellery	< 130 $\mu\text{g g}^{-1}$	Canadian Minister of Justice (2018)
Metal-Containing Jewelry Law	Jewellery	< 300 $\mu\text{g g}^{-1}$	Department of Toxic Substances Control (2012)
ASTM F963-17	Toys	< 75 $\mu\text{g g}^{-1}$ migratable Cd	US Consumer Product Safety Commission (2018)
Directive 84/500/EEC	Cooking ware ceramics	< 100 $\mu\text{g L}^{-1}$ migratable Cd	Council of the European Communities (1984)
	Hollow-ware ceramics	< 300 $\mu\text{g L}^{-1}$ migratable Cd	
California Proposition 65	Lip area of ceramics and glassware for food	< 800 $\mu\text{g g}^{-1}$	Office of Environ. Health Hazard Assess (2016)
Regulation 2016/217	Consumer paints	< 100 $\mu\text{g g}^{-1}$ or < 1000 $\mu\text{g g}^{-1}$ (where Zn > 10%)	European Union (2016)
Directive 94/62/EC	Packaging and packaging waste	< 100 $\mu\text{g g}^{-1}$ ^b	European Parliament and Council of the EU (1994)

^a Except where coloured for safety or where recycled PVC used

^b The limit applies to the sum of Cd, Hg, Pb and Cr VI concentrations, except for recycled materials in controlled, closed loop products

Table 2: Number of cases in which Cd was detected among the different categories of plastic consumer products and components tested by XRF, along with summary statistics defining its concentration (in $\mu\text{g g}^{-1}$). Also shown are the occurrence of Cd in PVC-based plastic samples and its (suspected) presence in pigmented form.

Descriptor	Food-contact	Storage and construction	Clothing and accessories	Toys and hobbies	Office and garden	EEE	Total
<i>n</i>	10	17	9	43	12	20	111
mean	79.6	1670	4100	3270	1490	266	2050
median	67.5	488	124	407	358	153	209
min	27.2	18.6	35.3	36.3	21.1	18.8	18.6
max	148.4	10,000	35,000	19,600	13,400	1,370	35,000
<i>n</i> PVC	0	5	0	10	1	1	17
<i>n</i> pigmented	0	2	0	21	1	0	24

Table 3: Details of plastic samples in which Cd was suspected to be present in pigmented form, along with concentrations of Cd and Se (nd = not detected). Shown in parentheses are concentrations of migratable Cd determined according to European Standard EN 71-3.

product	sample	colour	manufacturer	date	Cd, $\mu\text{g g}^{-1}$	Se, $\mu\text{g g}^{-1}$
ballcock	float valve	orange	Ideal Standard	1970s	2360	189
stapler	handle	red	unknown	1990s	13,400	3360
Venetian blind	slat	red-brown	unknown	unknown	8,221	905
"Mousey Mousey"	games cup	orange	Spears	1983	2470 (0.83)	335
"Connect 4"	counter	red	MB Games	1984	2500 (6.6)	632
Shape sorter	shape	yellow	Tupperware	1970s	8950 (10.2)	nd
"Sorry" board game	figure	yellow	Waddingtons	1970s	2060	nd
	figure	red			1120	nd
"Weebles"	figure	red	Airfix	1970s	1950	420
	figure	pink			592	nd
various construction sets	brick	yellow	Lego	1970s	15600 (61.7)	nd
	brick	yellow			8940	nd
	brick	red			19600 (221)	2920
	brick	red			16300 (145)	2700
	brick	yellow			13500 (98.0)	nd
	brick	yellow			17400	nd
	cog	yellow			12100	nd
"Smurf" set	figure	red	Schleich	1979	648 (30.5)	nd
"Playmobil" set	figure	yellow	Geobra Brandstaetter	1974	8693 (33.3)	nd
	stretcher	red			242	nd
bucket	bucket handle	red	unknown	unknown	2310	538
construction kit	figure	yellow	unknown	unknown	303	nd
	figure	orange			236	nd

Table 4: Number of cases in which Cd was detected by XRF in the glaze of ceramics and in the enamels of decorated drinking glasses and decorated glass bottles, along with summary statistics defining its concentration (in $\mu\text{g g}^{-1}$).

	Ceramics (<i>n</i> = 174)	Drinking glassware (<i>n</i> = 197)	Glass bottles (<i>n</i> = 36)
<i>n</i>	87	134	11
mean	4420	11,400	6490
median	2920	8460	5670
min	46.6	285	1170
max	38,100	70,900	19,400

Table 5: Concentrations of total (interior) and extractable Cd in various items of hollow ware tested according to Directive 84/500/EEC. All volumes are approximately 350 ml except where noted and asterisks denote products that had been used before testing.

Type and interior colour(s)	Retailer/supplier	Cd-total, $\mu\text{g g}^{-1}$	Cd-extractable, $\mu\text{g L}^{-1}$
mug with spoon, red*	promotional gift	6070	0.32
mug, orange*	department store	2950	0.36
mug, orange-brown	hardware store	2700	0.05
stoneware mug, orange-brown	hardware store	1120	0.41
bone China mug, red-white (damaged)*	gift store	3770	7.29
mug, yellow*	gift store	1130	2.72
mug, red	supermarket	2920	1.82
mug, red	supermarket	4070	0.25
earthenware jug, brown (500 ml)*	secondhand store	38100	14.9
mug, red	supermarket	2890	0.01

Figure 1: A selection of Cd-pigmented toys analysed as part of the present study.



Figure 2: Concentrations of Cd versus concentrations of Se in different types of consumer product. Statistical results are derived from linear regression analysis (forced through the origin) of individual datasets and overall data; note that $p < 0.01$ in all cases.

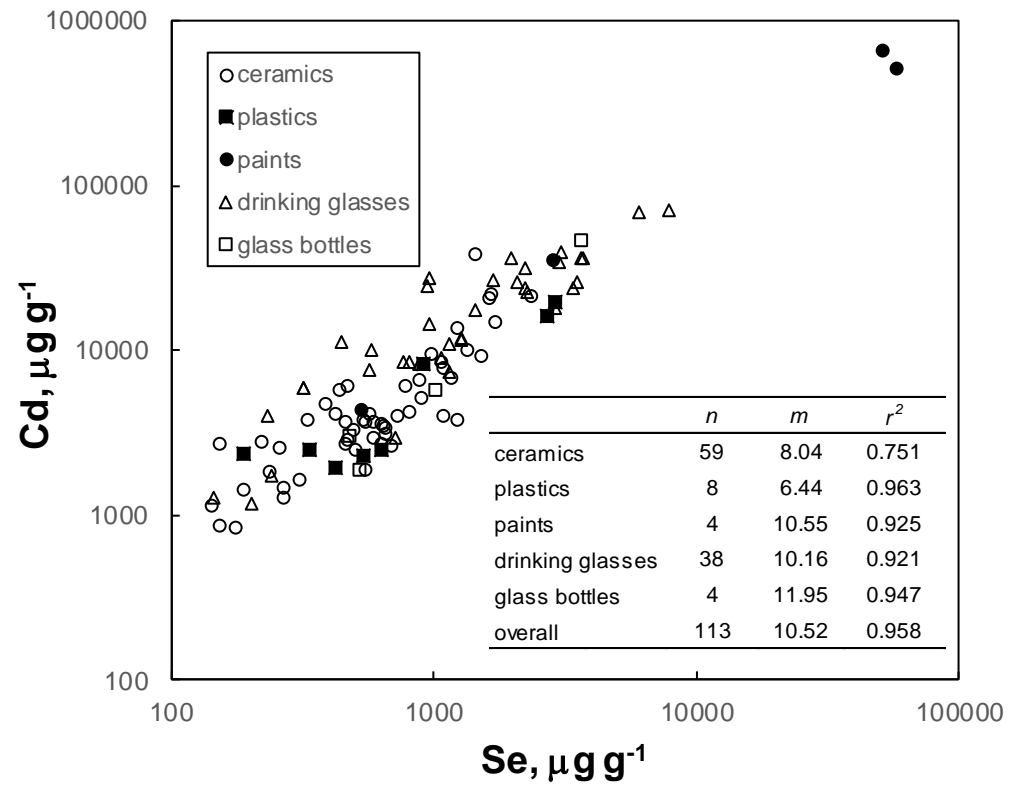


Figure 3: A selection of Cd-positive ceramic mugs and decorated drinking glasses and bottles analysed as part of the present study.



Figure 4: Spectra arising from the analysis of externally decorated areas (located in yellow) of a ceramic mug and high ball glass. Note the absence of the $Zr_{K\alpha}$ peak on the glass, indicating no encapsulation of pigmented Cd sulphoselenide.

