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**High levels of migratable lead and cadmium on
decorated drinking glassware**

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33 **Abstract**

34 Externally decorated glassware used for the consumption of beverages, purchased
35 new or sourced second-hand, and including tumblers, beer glasses, shot glasses, wine
36 glasses and jars, has been analysed for Pb and Cd by portable x-ray fluorescence
37 (XRF) spectrometry. Out of 197 analyses performed on distinctly different colours
38 and regions of enamelling on 72 products, Pb was detected in 139 cases and amongst
39 all colours tested, with concentrations ranging from about 40 to 400,000 $\mu\text{g g}^{-1}$
40 (median = 63,000 $\mu\text{g g}^{-1}$); Cd was detected in 133 cases and amongst all colours apart
41 from gold leaf, with concentrations ranging from about 300 to 70,000 $\mu\text{g g}^{-1}$ (median
42 = 8460 $\mu\text{g g}^{-1}$). The frequent occurrence of these metals is attributed to their use in
43 both the oxidic fluxes and coloured pigments of decorative enamels employed by the
44 glass industry. A standard test involving extraction of the external surface to within 20
45 mm of the rim (lip area) by 4% acetic acid and subsequent analysis by ICP was
46 applied to selected positive samples ($n = 14$). Lead concentrations normalised to
47 internal volume exceeded limit values of 0.5 mg L^{-1} in all but one case, with
48 concentrations over 100 mg L^{-1} returned by three products. Cadmium concentrations
49 exceeded limit values of 4 mg L^{-1} in five cases, with a maximum concentration of
50 about 40 mg L^{-1} . Repeating the experiment on five positive samples using a
51 carbonated drink (Coca Cola Classic) resulted in lower extractable concentrations but
52 non-compliance for Pb in all cases. The presence of high concentrations of total and
53 extractable Pb and Cd in the decorated lip areas of a wide range of products
54 manufactured in both China and Europe is cause for concern from a health and safety
55 perspective.

56

57 **Keywords:** glassware; decorative enamel; XRF; lead; cadmium; migration

58

59 **1. Introduction**

60 Because many heavy metals are able to induce acute and chronic toxicity at low
61 doses, there have been efforts to reduce human exposure through both a progressive
62 decrease in their use in consumer products and increasingly stringent environmental
63 regulations. Since ingestion is one of the principal routes of exposure, a particular
64 concern is the use of harmful metals in products that are designed or have the
65 potential to come into contact with food, like packaging, storage containers, crockery
66 and cutlery, kitchen utensils and ovenware (Weidenhamer et al., 2017).

67

68 Among food contact materials, ceramicware has been the focus of much attention
69 over the past few decades because of the use of various heavy metals and metalloids
70 in its finishing (Ajmal et al., 1997; Sheets et al., 1999; Henden et al., 2011; Dong et
71 al., 2015). Here, the glaze usually consists of a frit-clay suspension combined with a
72 metallic oxide flux that reduces the softening temperature of the various components,
73 while decorative enamel or metal (e.g. gold leaf) may be applied either before firing
74 (underglaze) or on top of the glaze before re-firing at a lower temperature. Being a
75 powerful flux and an effective solvent for other glaze components, coupled with a
76 wide processing latitude, PbO remains a favourable component of ceramicware glaze,
77 despite lead-free replacements having been developed (Beldi et al., 2016). Regarding
78 decoration, colour pigments are limited to those that are thermally stable during firing,
79 with a greater range available for lower temperature overglazing. Popular pigments

80 yielding brilliant colours include chrome oxide (green), zirconium vanadium blue and
81 cadmium sulphoselenides (red) (Lehman, 2002).

82

83 In theory, the migration of hazardous metals from the ceramic surface, like Pb and Cd,
84 should be extremely low unless the glaze is incorrectly formulated or fired. Although
85 improper applications have resulted in isolated cases of acute metal poisoning from
86 food in contact with ceramicware (Zuckerman et al., 1989; Ziegler et al., 2002), many
87 impacts of heavy metals arise from the accumulation of low doses over decadal time
88 frames that are difficult to attribute to a specific source (Mead, 2010; Zhao et al.,
89 2012). To this end, regulatory bodies have set compliance limits based on Pb and Cd
90 migratability from the interior of ceramicware by 4% acetic acid for 24 h and as
91 stipulated by European Communities Directive 84/500/EEC (Council of the European
92 Communities, 1984); currently, the respective limits are 4.0 and 0.3 mg L⁻¹, but
93 proposals to radically reduce them to 10 and 5 µg L⁻¹ and to incorporate limits for
94 other hazardous elements, including As, Cr and Sb, are presently under discussion by
95 the European Commission (Beldi et al., 2016).

96

97 Externally decorated glass hollow-ware intended for beverages is generally
98 overglazed, with a migratability test and maximum limits adopted voluntarily by the
99 glass industry that are limited to the area within 20 mm of the rim and where direct
100 contact with the lips occurs (ASTM, 2009). Despite the availability of such a test,
101 coupled with well-publicised recalls of decorated glasses intended for children
102 because of the presence of Cd-based paint (Mead, 2010), there has been no systematic
103 investigation into the nature of the decorative materials employed by the industry and
104 the potential for consumer exposure to hazardous elements. To the author's

105 knowledge, the only published scientific study in this respect compared the migration
106 of Pb and Cd from the lip areas of decorated, food-contact ceramicware and glassware
107 available on the Polish market (Rebeniak et al., 2014); thus, while most ceramicware
108 was compliant, with the metals undetected in many cases, about 20% of glassware
109 tested ($n = 393$) was non-compliant with respect to national regulations.

110

111 In order to better understand the composition and leachability of decorated exterior
112 surfaces of consumer glassware intended for the consumption of beverages, the
113 present study combines non-destructive elemental analysis with the current ATSM
114 migration test. Specifically, the surfaces of a range of products purchased new and
115 sourced second-hand are probed for Pb and Cd, both spatially and according to colour,
116 by portable x-ray fluorescence (XRF) spectrometry, while acetic acid-extracts of
117 selected decorated lip areas are analysed for the metals by inductively coupled plasma
118 (ICP) spectrometry.

119

120 **2. Materials and methods**

121 *2.1. Sampling and sample categorisation*

122 Excluding replicates, a total of 72 glass products used to drink from directly and that
123 had been enamel-decorated on part of the exterior were considered in the present
124 study. New glassware was purchased in April and May 2017 from local supermarkets
125 ($n = 10$), homeware stores ($n = 11$) and gift shops ($n = 17$), while older items were
126 purchased from second-hand (charity) shops ($n = 15$) or were borrowed from
127 colleagues but originally purchased in the UK ($n = 19$). Samples were categorised
128 according to type or function as highball ($n = 15$), lowball ($n = 8$), mug ($n = 3$), beer
129 ($n = 16$), shot ($n = 21$), wine-cocktail ($n = 4$) or jar ($n = 5$), with items in the latter

130 category characterised by distinctly thicker (soda-lime) glass and a screw-cap lid.
131 Individual products were photographed and the internal volume, minimum distance of
132 decorative enamel to the rim and dominant colours of application recorded. The
133 estimated coverage of the external surface that was decorated (as a percentage and
134 excluding the base) and, where stated, country of manufacture were also noted.

135

136 *2.2. Sample analysis*

137 Samples were analysed by portable XRF spectrometry using a Niton XL3t 950 He
138 GOLDD+ for a suite of elements, of which Pb and Cd as hazardous and/or restricted
139 metals are the focus of the present study. Where possible, samples were contained by
140 a 4000 cm³ Thermo Fisher Scientific accessory test stand (PN 420-017) with the XRF
141 securely fitted nose-upwards to the baseplate of the stand and operated remotely from
142 a laptop. For glassware too large to be contained by or repositioned within the test
143 stand, analyses were performed handheld and on a stainless steel table, cushioning the
144 samples on a folded lead apron and securing them between a number of suitably solid
145 and attenuating objects.

146

147 The study made use of the instrument's 'small-spot' facility (3-mm collimation) in
148 order to spatially probe decorated areas of distinctly different colour. Thus, with the
149 sample illuminated by an LED mounted above the XRF detector, real-time imagery
150 from an adjacent CCD camera, coupled with a circular reticule defining the small-
151 spot, are projected to the laptop, allowing the operator to accurately position the
152 sample with respect to the area being examined.

153

154 Once positioned, enamelled surfaces were analysed in a low-density plastics mode
155 with thickness correction (decorated layers were assumed to extend to a depth of 0.05
156 mm) for 45 seconds, comprising periods of counting of 30 seconds at 50 kV and 40
157 μA and 15 seconds at 20 kV and 100 μA . Spectra were quantified by fundamental
158 parameters to yield elemental concentrations on a dry weight basis (in $\mu\text{g g}^{-1}$) and a
159 counting error of 2σ (95% confidence).

160

161 2.3. *Quality assurance*

162 Measurement limits of detection, defined as three counting errors and derived from
163 the analysis of the unenamelled glass substrates of 14 samples housed in the test
164 stand, averaged (\pm one standard deviation) 27 ± 9.4 and 215 ± 13 $\mu\text{g g}^{-1}$ for Pb and Cd,
165 respectively, in the plastics mode. Repeated analyses of the same decorated area on
166 eight different samples revealed a precision (as relative standard deviation, rsd) that
167 was better than 10% for both elements; multiple analyses of the same décor but at
168 different locations resulted in rsds that were usually similar to those defining the
169 respective precisions, but greater variability occurred when the surface under
170 examination was too small to be completely encapsulated by the reticule. Analysis of
171 the same decorated areas of replicate highball glasses purchased from a gift shop ($n =$
172 4) revealed rsds of up to 20% for both metals, presumably reflecting additional
173 variations arising from differences in the precise content and thickness of the
174 enamelled applications between or within product batches.

175

176 The performance of the XRF in the plastics mode and with 3-mm collimation was
177 verified by the regular analysis of 13-mm thick Niton polyethylene discs impregnated
178 with Pb and Cd (PN 180-554, batch SN PE-071-N; PN 180-619, LOT#T-18), with

179 mean measured concentrations returned that were always within 10% of mean
180 certified values. As an additional measure of instrument performance on thin layers,
181 six standard reference paint films certified for Pb concentrations on an areal basis
182 (SRM 2570 to 2575; National Institute of Standards & Technology) and uniformly
183 coloured enamelled surfaces of selected glassware samples were analysed at the same
184 locations using both the plastics mode and a lead paint mode (the latter operating at 50
185 kV and 40 μA and without collimation). Concentrations of Pb in the reference films
186 returned in $\mu\text{g cm}^{-2}$ using the lead paint mode were within 10% of corresponding
187 certified values and were highly correlated with concentrations returned in the plastics
188 mode on a weight basis ($n = 6$; $r = 0.980$), with a slope, derived from linear regression
189 analysis, of $40.0 \text{ cm}^2 \text{ g}^{-1}$ and that was valid to a Pb concentration of at least 150,000
190 $\mu\text{g g}^{-1}$ on a weight basis. Concentrations of Pb returned by both modes on the
191 enamelled sample surfaces were also highly correlated ($n = 18$; $r = 0.926$) with a slope
192 ($= 40.7 \text{ cm}^2 \text{ g}^{-1}$) that was almost identical to that defining the relationship in the
193 reference paint films.

194

195 2.4. *Extraction tests*

196 To evaluate the migratability of Pb and Cd from the externally enamelled surfaces of
197 drinking glassware, 14 items of varying source, type and colour whose metal-positive
198 décor extended to the lip area were subject to the ASTM (2009) standard extraction
199 test, with a shot glass decorated with Pb- and Cd-free enamelling serving as a control.
200 Thus, interior volumes to 6 mm from the rim were determined by addition of tap
201 water from a measuring cylinder before glassware was cleaned in detergent, rinsed
202 with distilled water and air-dried. Each sample was then marked on the exterior
203 substrate at the 20 mm level and placed, inverted, into an acid-cleaned 300 ml Pyrex

204 crystallisation dish or, for the largest items or those with handles, an acid-cleaned 1 L
205 Pyrex beaker. A solution of 4% glacial acetic acid (Fisher Scientific analytical grade)
206 at pH 2.6 was carefully added to each container from a polyethylene measuring
207 cylinder to the 20 mm mark on the sample exterior and the volume recorded. After
208 extraction for 24 h at room temperature and in the dark, 15 ml of acetic acid was
209 pipetted from each dish or beaker into a series of 50 ml screw-capped polypropylene
210 centrifuge tubes that were stored in a refrigerator at 4 °C pending analysis. Five
211 further samples, including duplicates of three products extracted in acetic acid, were
212 also extracted in a less aggressive carbonated beverage (Coca Cola Classic; pH = 2.6)
213 for 24 h and at room temperature using an otherwise identical protocol, with
214 centrifuge tubes stored likewise pending analysis. Meanwhile, enamelled surfaces of
215 the glassware subject to extraction were air-dried for 24 h before being examined for
216 physical modification and colour change and reanalysed by XRF as above.

217

218 Acetic acid and Coca Cola extracts were analysed for Pb (220.353 nm) and Cd
219 (228.802 nm) by ICP-optical emission spectrometry using a ThermoScientific iCAP
220 7400. The instrument was calibrated using four mixed standards and a blank prepared
221 by serial dilution of LabKings standard solutions (Hilversum, NL) in 2% HNO₃, with
222 settings as follows: exposure time = 2 s; RF power = 1150 W; nebuliser, coolant and
223 auxiliary gas flows = 0.50, 12 and 0.5 L min⁻¹, respectively; viewing height = 12 mm;
224 uptake time = 50 s; wash time = 15 s. Limits of detection, based on three standard
225 deviations about multiple measurements of blanks, were about 0.01 mg L⁻¹ for both
226 metals

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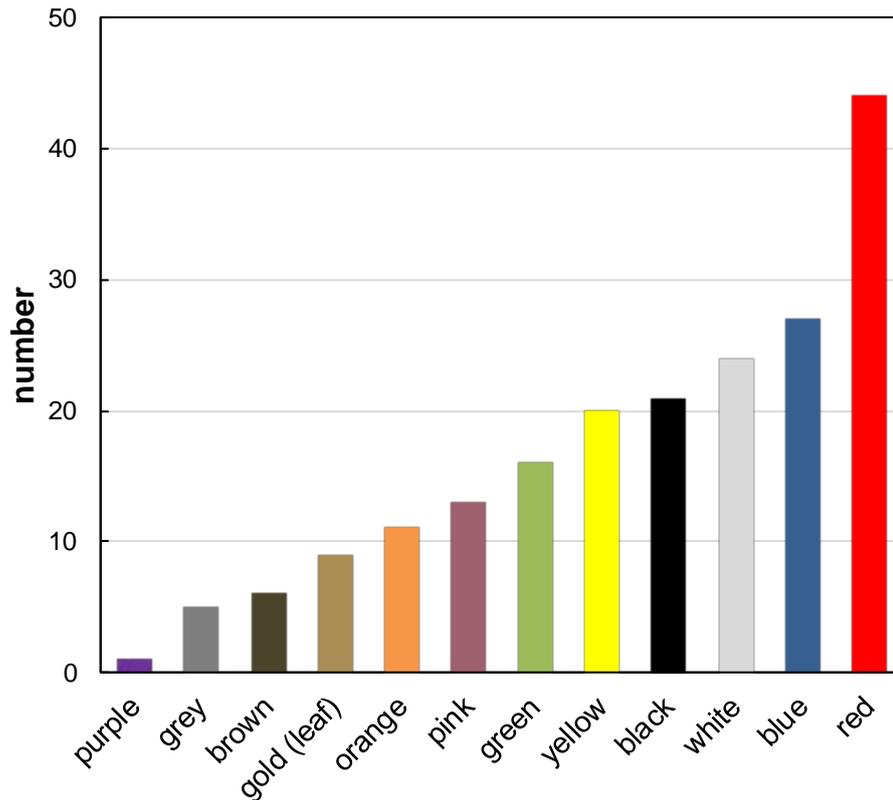
228 **3. Results**

229 *3.1. Sample characteristics*

230 The estimated, external coverage of decoration on glassware ranged from $\lesssim 5\%$ for
231 three beer glasses bearing small logos and volume markers to more than 90% for
232 several multi-coloured shot glasses. The minimum distance from the enamelled area
233 to the rim varied considerably, with several shot glasses bearing gold leaf on the rim
234 itself and some jars undecorated above 50 mm. A total of 36 samples had external
235 decoration within the 20 mm lip area, with a further 19 products having décor that
236 terminated at precisely this distance. Although the majority of the enamelled exteriors
237 appeared to be intact, albeit with different degrees of scratching and crazing, two
238 items purchased new and several second-hand items exhibited areas where the
239 application had deteriorated sufficiently to expose the underlying glass substrate,
240 while a number of items displayed isolated and coloured flecks contaminating parts of
241 the exterior that were otherwise enamel-free.

242

243 A total of 197 analyses were performed on the glassware using the plastics mode of
244 the XRF, with the distribution of colours examined summarised in Figure 1. While
245 some samples contained lettering, logos or patterns of a single colour, most glassware
246 was decorated in several colours that were either incorporated into images, characters,
247 cartoons or motifs or applied as discrete areas of repeating patterns, with gold leaf
248 sometimes used as a decorative border. The number of analyses per sample varied
249 (between 1 and 8) depending on the extent and complexity of the decorated surface
250 and limitations imposed by sufficient coverage and uniformity within the reticule
251 defining the primary x-ray beam area.



252

253 *Figure 1: Frequency distribution of the colours analysed on the decorated glassware.*

254

255 *3.2. Pb and Cd concentrations in decorative enamel*

256 The concentrations of Pb and Cd on a dry weight basis arising from the analyses of all
 257 decorated surfaces by XRF in the plastics mode analysed are summarised in Table 1,
 258 with the spatial and colour distribution of elemental concentrations on the exterior of a
 259 supermarket lowball tumbler exemplified in Figure 2. Overall, Pb was detected on
 260 139 decorated surfaces, or about 70% of those analysed, with concentrations spanning
 261 five orders of magnitude ($40 \mu\text{g g}^{-1}$ to about 40% by weight) and a median
 262 concentration of about $60,000 \mu\text{g g}^{-1}$. (On an areal basis, the range and median are
 263 equivalent to about 1 to $10,000 \mu\text{g cm}^{-2}$ and $1500 \mu\text{g cm}^{-2}$, respectively.) The metal
 264 was detected in all sample categories with the exception of jars and across all colours
 265 recorded (including the decorative gold leaf of some items), with 52 products out of a

266 total of 72 containing at least one colour that was Pb-positive. Items associated with
267 the surfaces containing Pb concentrations exceeding 10% by weight were sourced
268 both new and second-hand; however, of these, only two supermarket highball glasses
269 bearing red patterns and a gift store highball glass decorated with a cartoon were
270 labelled with the country of manufacture (and as Turkey, France and China,
271 respectively).

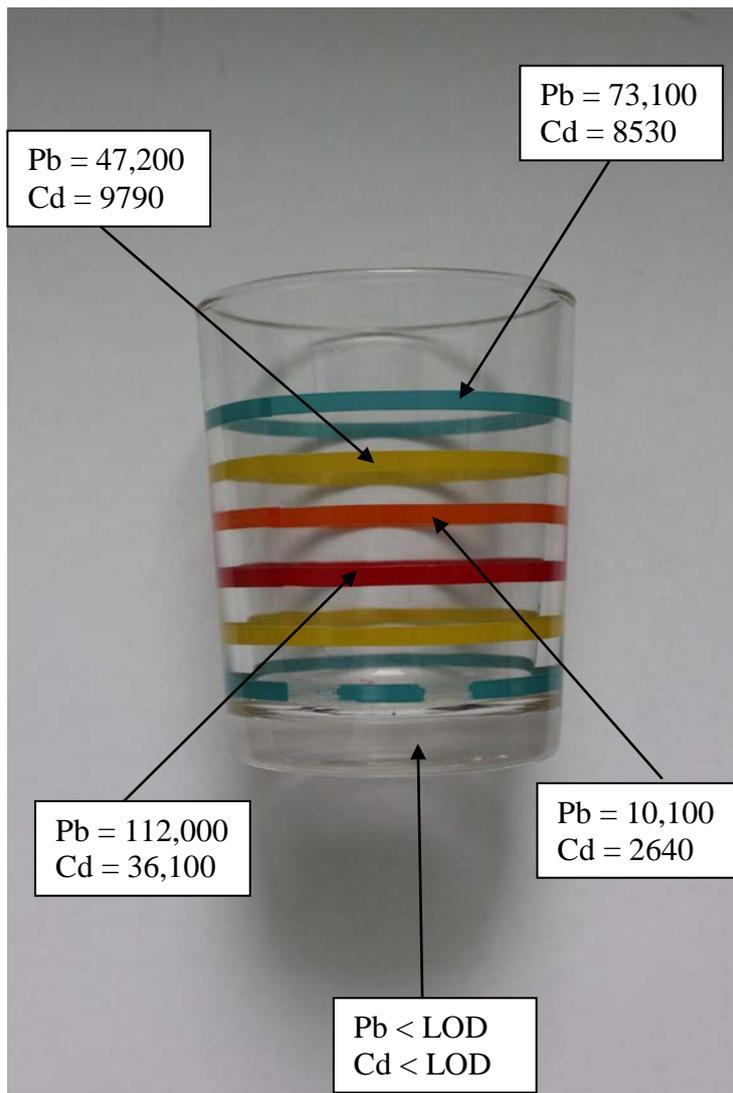


Figure 2: The distribution of Pb and Cd concentrations (in $\mu\text{g g}^{-1}$) on the exterior of a lowball tumbler purchased from a supermarket. Note the deterioration of the lowest (blue) ring, evident at the time of purchase.

272

273 Cadmium was detected in just under 70% of all decorated surfaces analysed, with
274 concentrations spanning more than two orders of magnitude and its occurrence
275 recorded in at least one colour on 51 products. The metal was encountered in
276 decorations applied to all sample categories with the exception of jars and, while the
277 highest concentrations were usually encountered in red enamel, Cd was present in
278 every decorative colour recorded with the exception of gold. There was no clear
279 difference in the distributions of Cd concentrations between new and second-hand
280 items, and while most Cd-positive samples, where indicated, were manufactured in
281 China, several purchased from various supermarkets were produced elsewhere. For
282 example, three different highball glasses adorning repeating red, blue or black patterns
283 and with Cd concentrations up to 26,000 $\mu\text{g g}^{-1}$ were manufactured in France, Turkey
284 and the UK, respectively.

285

286 *Table 1: Distributions and summary statistics of the concentrations of Pb and Cd in*
287 *the decorative enamels analysed (all concentrations in $\mu\text{g g}^{-1}$).*

	< LOD	< 10 ²	10 ² -10 ³	10 ³ -10 ⁴	10 ⁴ -10 ⁵	>10 ⁵	min.	max.	median
Pb	58	7		12	81	39	40	396,000	63,000
Cd	63		9	68	57		285	70,900	8460

288

289

290 Other potentially hazardous elements detected in glassware by XRF but not
291 considered in the present study included As, Cr, Sb and Se. Thus, once spectral
292 overlap from Pb had been accounted for (Pb-L α = 10.55 keV; As-K α = 10.54 keV),
293 As was encountered in 20 cases and at concentrations up to 100 $\mu\text{g g}^{-1}$. The presence
294 of similar concentrations of As in the underlying vitreous substrate, however, is
295 consistent with the occurrence of residual arsenic acid employed as an intermediate

296 fining agent in the manufacture of the glass itself. Chromium concentrations in the
297 decorated surfaces spanned three orders of magnitude and with a maximum
298 concentration of about 20,000 $\mu\text{g g}^{-1}$. Positive results were encountered on 41 items
299 and the metal exhibited a distinct bias towards dark, achromatic paints; specifically,
300 all but one grey and > 90% of black formulations contained Cr, with nine out of the
301 twelve highest measured concentrations of the metal encountered in the latter colour.
302 Although Cr was associated with Pb in 74 analyses, the two metals were not
303 significantly correlated, either overall or on an individual colour basis.

304

305 Antimony was detected in 23 decorated surfaces and at concentrations averaging
306 about 1000 $\mu\text{g g}^{-1}$ and, while its occasional presence in the substrate suggests a similar
307 role to As as a fining agent, it also appeared to be contained within several yellow and
308 orange decorated surfaces. Selenium was detected in 54 enamels from 40 samples,
309 with the highest concentrations (in excess of 1000 $\mu\text{g g}^{-1}$) encountered in brightly
310 coloured red and orange applications on a range of new and old items. Overall,
311 concentrations of Se were correlated with concentrations of Cd, where both elements
312 were detected ($n = 54$; $r = 0.863$; Se-Cd slope = 0.0831), and the correlation improved
313 when the statistical test was restricted to data defining the brightest colours listed
314 above ($n = 38$; $r = 0.921$; Se-Cd slope = 0.0915).

315

316 *3.2. Extraction of Pb and Cd from decorated surfaces*

317 The 20 mm lip area of samples that had been subject to acetic acid extraction for 24 h
318 usually exhibited a distinct fading and a reduction in sheen of the enamelled surface
319 that was most marked on the brighter colours and least noticeable on any gold leaf
320 décor. In a few cases, discolouration extended beyond the lip line suggesting that

321 acidic vapour was also able to react with some applications, while in one case, the
322 entire enamel within the lip area had completely corroded, resulting in an
323 accumulation of coloured particulates at the bottom of the extract. Samples subject to
324 extraction in Coca Cola exhibited limited but noticeable fading of colour of the
325 enamelled areas, with a reduction in sheen and brown staining also evident on some of
326 the paler colours. Significantly, a number of areas having undergone extraction shed
327 small quantities of material as a powder when subsequently dried and wiped with two-
328 ply blue roll.

Table 2: Quantities and volume-normalised concentrations of Pb and Cd extracted by acetic acid and Coca Cola from drinking glassware decorated within the lip area and as determined by ICP (Pb^{ext} and Cd^{ext} , respectively). Also shown are the estimated percentage of the lip area that is decorated, the colours in the lip area (in descending order of abundance) and California Proposition 65 compliance (x = Pb exceedance; + = Cd exceedance). Samples are numbered for the identification of corresponding percentage removals of Pb and Cd by acetic acid, ascertained by XRF and as illustrated in Figure 4, while common superscripted letters denote duplicate items tested by both acetic acid and Coca Cola extracts.

extract and sample no.	type	source	lip area decorated, %	colours within lip area	Pb ^{ext} , mg	Pb ^{ext} , mg L ⁻¹	Cd ^{ext} , mg	Cd ^{ext} , mg L ⁻¹	P65 compliance
<i>4% acetic acid</i>									
1	beer	supermarket	3	red	3.28	6.07	0.22	0.41	x
2	mug	homeware store	15	grey	26.42	88.07	0.04	0.14	x
3	shot	charity shop	20	green, white, red, gold	3.12	78.11	0.13	3.35	x
4	wine	charity shop	5	white	0.44	3.01	0.02	0.12	x
5	highball	homeware store	7	black	3.17	11.51	0.31	1.11	x
6	lowball	gift shop	5	black, yellow, red	4.42	16.08	0.43	1.56	x
7	shot ^a	charity shop	10	green, brown, yellow	4.34	86.80	0.65	13.05	x +
8	shot	charity shop	10	black, red, green	8.36	167.29	0.81	16.26	x +
9	highball	supermarket	5	blue	0.48	1.73	0.04	0.15	x
10	shot	charity shop	20	white, gold, red	13.93	309.47	1.71	38.09	x +
11	lowball	charity shop	10	white, red, gold	3.71	18.53	0.25	1.23	x
12	highball ^b	gift shop	70	green, white, orange, black	33.83	123.03	4.00	14.53	x +
13	beer	charity shop	3	blue, yellow, black, red	0.03	0.08	<0.01	0.01	
14	mug ^c	homeware store	15	red	16.28	54.27	5.43	18.10	x +
15	shot (control)	gift shop	75	green, blue, white	<0.01	<0.01	<0.01	<0.01	
<i>Coca Cola Classic</i>									
7	shot ^a	charity shop	10	green, brown	0.07	1.39	0.15	2.92	x
16	shot	charity shop	25	gold, white, red	0.04	0.87	0.04	0.90	x
17	shot	charity shop	15	white, red, yellow	0.09	2.27	0.08	2.08	x
12	highball ^b	gift shop	70	green, white, orange, black	0.19	0.69	0.17	0.63	x
14	mug ^c	homeware store	15	red	0.16	0.53	0.38	1.28	x
15	shot (control) ^d	gift shop	75	green, blue, white	<0.01	<0.01	<0.01	<0.01	

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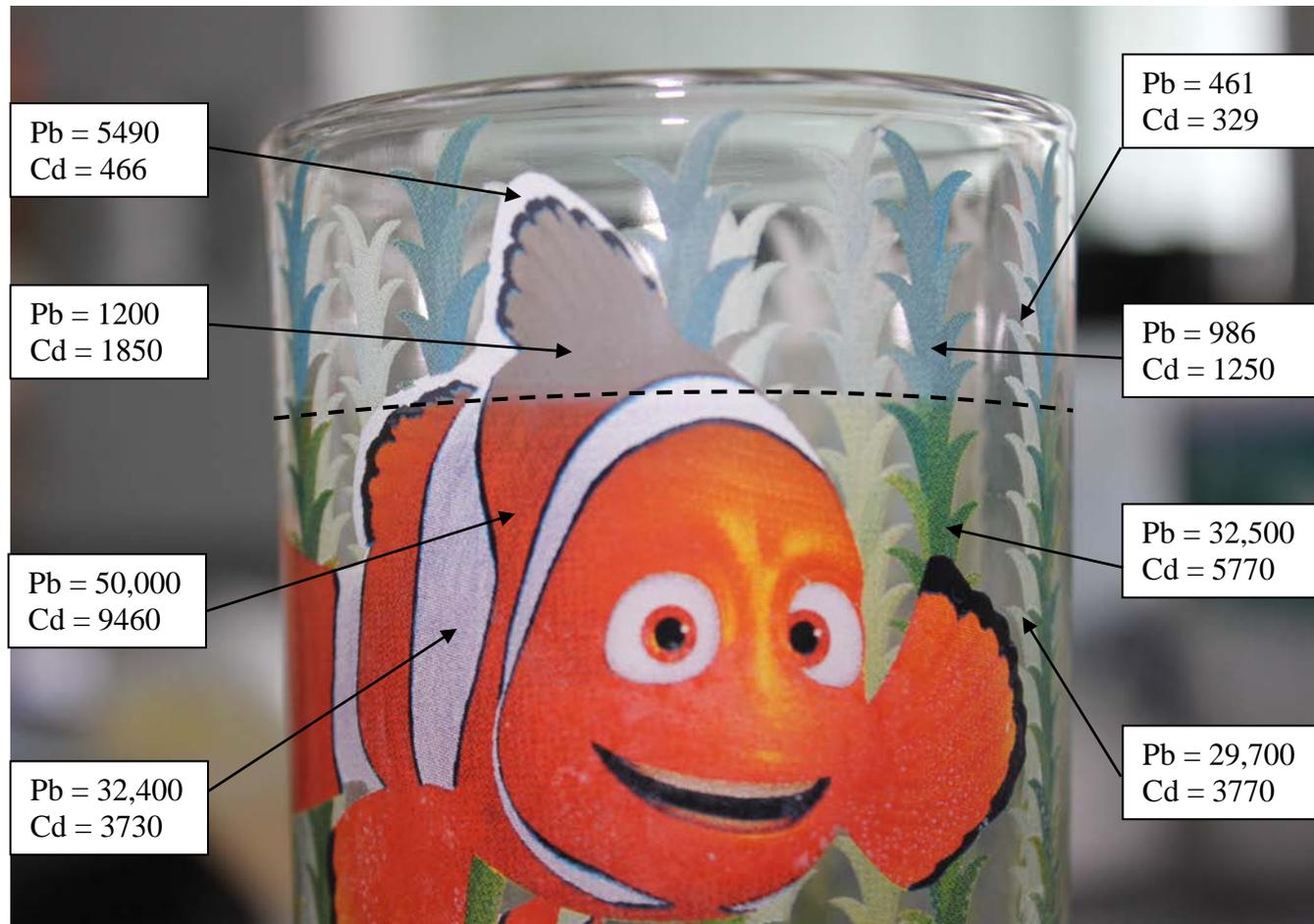
331 *Figure 3: The distribution of Pb and Cd concentrations (in $\mu\text{g g}^{-1}$) on a highball glass purchased from a gift shop (sample 12 in Table 2) and*
332 *after undergoing acetic acid extraction of the lip area that is defined by the dashed line. Note the distinct colour changes and reductions in*
333 *elemental concentrations effected by the acid.*

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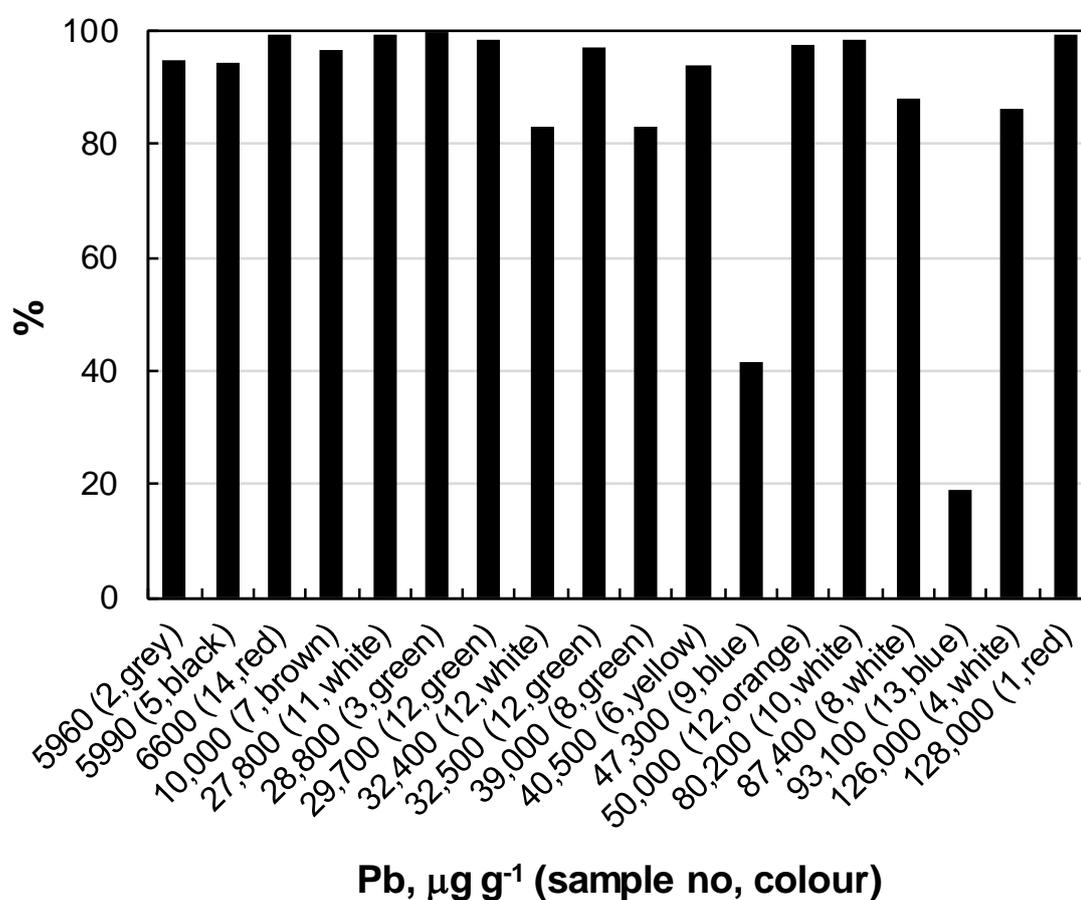
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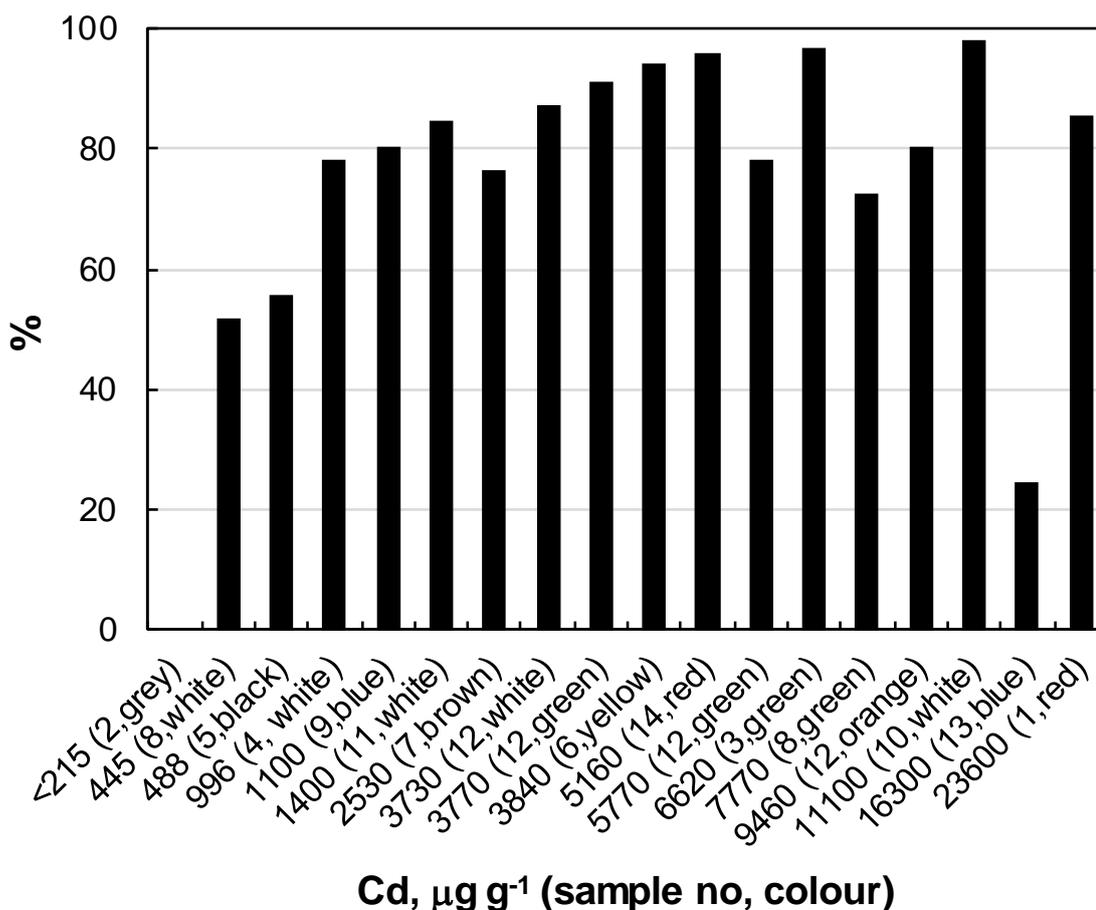
337



338 Figure 4: The percentage removal of Pb and Cd from the lip area of selected positive
 339 samples, calculated from the difference in concentrations of the same decorated area
 340 determined by XRF before and after acetic acid extraction and shown as a function of
 341 (increasing) initial concentration. Note that, in total, results arising from the analysis
 342 of 18 decorated areas from 14 different samples are shown, whose identification
 343 (corresponding to the samples numbers in Table 2) and colours tested are given in
 344 parentheses.



345



346

347

348 The visual and chemical impacts of acetic acid extraction of the lip area are
 349 exemplified in Figure 3 for a colourful, child’s highball glass purchased from a gift
 350 shop. Here, bright orange and green have faded to grey and pale blue, respectively,
 351 while concentrations of Pb and Cd are often more than an order of magnitude lower
 352 within the lip area compared with equivalent areas of the same original colour below
 353 the 20 mm line. The percentage removal of Pb and Cd from all lip areas tested with
 354 acetic acid and determined more precisely by XRF analysis of the same locations on
 355 the glassware before and after extraction is shown in Figure 4, with details of
 356 individual samples analysed given in Table 2. Regarding Pb, removal exceeded 80%
 357 for all positive surfaces tested ($n = 18$) and across a wide range of initial
 358 concentrations with the exception of a beer glass (~ 20%) and highball tumbler (~ 40

359 %) whose lip areas were decorated in blue. For Cd, removal exceeded 50% for all
360 positive areas tested ($n = 17$) and regardless of initial concentration on a weight basis
361 with the exception of a blue motif close to the rim of a beer glass (about 25%
362 extraction). In contrast, and despite visible discolouration of and material loss from
363 the enamelled lip areas subject to extraction in Coca Cola for 24 h, elemental
364 concentrations measured by XRF before and after revealed no differences beyond the
365 counting errors of the instrument or errors arising from replicate readings.

366

367 The quantities and concentrations of Pb and Cd in the acid and Coca Cola extracts
368 themselves (Pb^{ext} or Cd^{ext}) and as determined by ICP are shown in Table 2. Here,
369 extractable concentrations are normalised with respect to internal volume; that is, the
370 quantity of metal released from the exterior lip area is divided by the volume
371 contained to 6 mm below the rim. Among the products tested, concentrations are
372 highly variable, reflecting differences in the degree of decoration within the lip area,
373 the nature of the enamelling and the ratio of external surface area to internal volume;
374 overall, however, concentrations are lower in Coca Cola extracts than in acetic acid
375 extracts (see concentrations in duplicate samples subject to both types of extraction).
376 Specifically, concentrations of Pb^{ext} range from undetected ($< 0.01 \text{ mg L}^{-1}$) in both
377 controls to more than 100 mg L^{-1} for two second-hand, multi-coloured shot glasses
378 and a highly decorated highball glass purchased from a gift shop (and illustrated in
379 Figure 3) when extracted in acetic acid. Concentrations of Cd^{ext} range from
380 undetected ($< 0.01 \text{ mg L}^{-1}$) in the controls and a multi-coloured beer glass extracted in
381 acetic acid to greater than 10 mg L^{-1} in acetic extracts of various colourful, second-
382 hand shot glasses, the highball glass referred to above and a mug bearing red rings
383 around the entire circumference sourced from a homeware store.

384

385 **4. Discussion**

386 *4.1. Nature of Pb and Cd in the enamelled glassware*

387 The widespread occurrence of Pb in the enamelling of glassware used to consume
388 beverages is consistent with the pervasive application of PbO in the flux to lower the
389 melting point of the glass-forming components (Beldi et al., 2016). That adjacent
390 areas of different colour on the same item often contained Pb concentrations that
391 differed by about an order of magnitude, however, suggests leaded pigments are also
392 employed in the enamelling process. These include the brightly coloured lead
393 antimonide (yellow) and lead chromates (yellow-orange-red), and green chromic
394 oxide, produced by the thermal decomposition of PbCrO₄ (Lehman, 2002).

395

396 Cadmium pigments, and in particular Cd sulphoselenides, are particularly favourable
397 for enamelling because they produce a range of brilliant reds, oranges and yellows
398 which are able to withstand high processing temperatures (Lehman, 2002). While the
399 highest concentrations of Cd were generally observed among bright red surfaces of
400 glassware and in association with Se, the metal was detected across a wide range of
401 chromatic and achromatic colours and where there was no evidence of interferences
402 through layering or encapsulation of non-target areas within the reticule. It is possible,
403 therefore, that CdO is present in the enamels more generally as a stabiliser or a
404 component of the flux itself (Hamer and Hamer, 2004; Demont et al., 2012).

405

406 *4.2. Regulatory compliance of enamelled glassware*

407 Legislation in Europe relating to Pb in paint can be traced back more than a century,
408 with concentration limits in consumer formulations being progressively revised

409 downwards (Bodel, 2010). Because high quality and cost-effective alternative
410 pigments and driers are now available, the current maximum concentration for Pb in
411 consumer paints and enamels is $90 \mu\text{g g}^{-1}$ in the dry film in many countries (Gottesfeld
412 et al., 2014). With regard to lead chromates, the EU has recently constrained their
413 availability to certain professions and industries and restricted the supply to one
414 particular company based in Canada (REACH, 2016). While there has been less
415 documentation of the content and effects of Cd in paints, the metal is currently
416 restricted by Annex XVII of REACH to a concentration of $100 \mu\text{g g}^{-1}$ in consumer
417 paints with the exception of formulations containing more than 10% Zn, and to 1000
418 $\mu\text{g g}^{-1}$ on painted articles (Commission Regulation, 2016).

419

420 Since hazardous elements employed in the flux or as a pigment are fused to a vitreous
421 substrate during kiln-firing they are not as accessible as when contained in unglazed
422 paint applications that can be readily scraped or dislodged. Accordingly, California's
423 Proposition 65, relating to the exposure of toxic chemicals to the public, has provided
424 higher limits of Pb and Cd concentrations in the decorated surfaces of food and
425 beverage glassware than in consumer paints; where products breach these limits, they
426 may still be sold within the state but a clear warning on the item or its packaging is
427 required (Office of Environmental Health Hazard Assessment, 2016). Specifically,
428 exterior decorations excluding the lip area must only utilise materials that contain \leq
429 $600 \mu\text{g g}^{-1}$ Pb and $4800 \mu\text{g g}^{-1}$ Cd, while exterior decorations extending into the lip
430 area must only employ materials that contain $\leq 200 \mu\text{g g}^{-1}$ Pb and $\leq 800 \mu\text{g g}^{-1}$ Cd. On
431 this basis, 49 out of the 72 samples considered in the present study would require a
432 warning regarding the Pb and/or Cd content on the exterior decoration, with 34
433 samples requiring a warning based on the Pb and/or Cd content in the lip area alone.

434 Non-compliant samples include both old and new products that encompass all
435 categories of drinking glassware with the exception of jars.
436
437 Extractable concentration limits for the lip area and based on immersion in 4% acetic
438 acid are also stipulated by Proposition 65 as 0.5 and 4 mg L⁻¹ for Pb and Cd
439 respectively (Calderwood and Bopp, 2005). With reference to Table 2, all but one
440 item tested (excluding the control) would be non-compliant and require a warning
441 label based on acid-extractable Pb, while five items, including two purchased new,
442 would require a warning based on extractable Cd. Despite concentrations of Pb
443 extracted by Coca Cola being significantly lower than those mobilised by acetic acid
444 (presumably because lead phosphate is considerably less soluble than lead acetate),
445 the Proposition 65 limit was exceeded in all cases for this extractant with the
446 exception of the control; in contrast, although release of Cd was less dependent on the
447 extraction medium, concentrations mobilised by Coca Cola were always below the
448 Proposition 65 limit.

449
450 While some countries have recently adopted similar, volume-normalised
451 concentration limits for the acid-extraction of Pb and Cd from the lip area of
452 decorated drinking glasses (e.g. Health Canada, 2016), others have defined safety
453 requirements on mass limits on metal migration. For instance, in Poland, and
454 according to PN-B 13210:1997, the total quantity of Pb or Cd extracted by 4% acetic
455 acid per product must not exceed 2 mg and 0.2 mg, respectively (Rebaniak et al.,
456 2014). On this basis, and according to Table 2, all but three items tested accordingly
457 in the present study (excluding the control) would be non-compliant for Pb (with

458 many samples releasing more than 10 mg), and all but five items would be non-
459 compliant for Cd (with a maximum migration of over 5 mg).

460

461 *4.3. The wider problem*

462 According to the Federation of European Screen Printers Associations, organic inks
463 that adhere to glassware are becoming more popular than metallic pigments that are
464 fused to the surface because of environmental concerns regarding the latter (Kiddell,
465 2015). Given that safer alternative colourants and fluxes are available to the industry,
466 and were evident on a number of newly-purchased Pb- and Cd-negative products
467 analysed herein, the overall results of this study are both surprising and concerning.
468 Why are harmful or restricted elements employed so commonly to decorate
469 contemporary glassware intended for beverage consumption that is manufactured not
470 only in China but also within the European Union and elsewhere? Additional analyses
471 performed with the XRF confirmed that hazardous elements are also used to decorate
472 a wider range of consumer glassware that has the potential to be in contact with food,
473 including the exteriors of bottles for the storage of beer, wine or spirits, the external
474 text and logos on egg cups, Pyrex jugs and measuring cups, and the undersides of
475 coasters and chopping boards.

476

477 The presence of hazardous elements in decorated glassware has implications for both
478 human exposure and the environment. Regarding the former, direct ingestion may
479 occur through the consumption of beverages in drinkware that is decorated within the
480 lip area, with exposure accentuated for hot or acidic drinks and for enamel that is
481 deteriorating; of particular concern in this respect is densely decorated glassware that
482 is specifically designed for use by children (e.g. see Figure 3). Indirect ingestion may

483 also occur via the handling of enamelled surfaces or through contamination of other
484 food-contact items should surfaces be abraded during washing or stack-storage.
485 Persistent use of a dishwasher is also known to cause decorative enamels to ‘fade’, but
486 a warning to this effect was stated on the packaging of only about one half of the
487 drink-ware products purchased new. With respect to the environment, the recycling of
488 decorated container glass like bottles and jars acts to introduce hazardous elements
489 into the post-consumer cullet, while landfilling of decorated drinking glassware that
490 cannot be recycled affords a means by which these elements enter groundwater
491 through leaching.

492

493 **5. Conclusions**

494 The present study has revealed high levels of the heavy metals, Pb and Cd, in the
495 external decorative enamelling of drinking glassware sourced both new and second-
496 hand in the UK. Significant quantities of the metals in the 20-mm lip area are
497 mobilised by acetic acid according to a standard test and by the popular soft drink,
498 Coca Cola Classic. From a health perspective, of greatest concern is the presence of
499 Pb and Cd in decorative enamelling within the lip area of children’s glassware
500 because of the potential for mobilisation and ingestion of small quantities of metal
501 over an extended period of time. Regarding end-of-life products, recycling risks
502 contaminating the post-consumer glass cullet, while disposal has the potential to
503 contaminate the environment. Consumers should be made aware of the presence and
504 mobility of Pb and Cd in decorated drinkware, while retailers and the glass industry,
505 with safer alternative pigments and fluxes available, have the responsibility to
506 eliminate toxic metals from decorated products. More generally, greater and clearer

507 regulatory oversight of chemicals that have immediate or long-term impacts on human
508 health is called for.

509

510

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515

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