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# Heavy Metals in the Glass and Enamels of Consumer Container Bottles

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1           **Heavy metals in the glass and enamels of consumer container bottles**

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15  
16           **Abstract**

17   The glass and enamelled decorations of bottles of alcoholic beverages sourced from retailers in the  
18   UK were analysed by x-ray fluorescence spectrometry for various heavy metals. In the glass  
19   substrate, lead, cadmium and chromium were present at concentrations up to about 1100  $\mu\text{g g}^{-1}$ ,  
20   1100  $\mu\text{g g}^{-1}$  and 3000  $\mu\text{g g}^{-1}$ , respectively, but their environmental and health risks are deemed to be  
21   low significance. Of more concern from an environmental and, potentially, occupational exposure  
22   perspective are the concentrations and mobilities of Pb and Cd in the enamels of many bottles. Thus,  
23   Pb concentrations up to about 100,000  $\mu\text{g g}^{-1}$  were found on the décor of various wine bottles and a  
24   beer bottle, and Cd concentrations of up to 20,000  $\mu\text{g g}^{-1}$  were measured in the decorated regions  
25   on a range of spirits, beer and wine bottles. Moreover, maximum concentrations that leached from  
26   enamelled glass fragments according to a standard test that simulates water and other liquids  
27   percolating through a landfill were about 1200 and 3200  $\mu\text{g L}^{-1}$  for Pb and Cd, respectively, with

28 several fragments exceeding the US Model Toxins in Packaging Legislation and, therefore, defined as  
29 “hazardous”. Given that safer decorative alternatives are available and that a precautionary principle  
30 should be adopted for toxic heavy metals, the pervasive use of Pb and Cd in the enamels of  
31 consumer bottles is brought into question.

32

33

#### 34 **Introduction**

35 Lead (Pb), cadmium, hexavalent chromium (Cr(VI)) and mercury (Hg) are highly toxic heavy metals  
36 that have come under intense scientific and medical scrutiny and increasing regulation over the past  
37 three decades (1-3). Restrictions are in place for the concentrations or mobilities of these metals in  
38 various consumer products, including toys, electronic equipment, ceramic products and other food-  
39 contact articles, jewellery, and paints, principally in order to protect human health and the  
40 environment (4-6). An additional rationale for limiting heavy metals in new consumer goods is to  
41 minimise the scope for introducing harmful chemicals into the recycling stream (7). However,  
42 inefficient or illegal practices have ensured that the recyclate may be contaminated by older (or  
43 sometimes newer) products that are not compliant with current regulations. As an example, there is  
44 widespread and low level dispersion of flame retardants, metalloids and metals in many plastic  
45 products recycled from improperly sorted or screened electronic waste (8).

46 Packaging is an important contributor to the solid waste stream, and the Packaging and Packaging  
47 Waste Regulations (9) set out to restrict heavy metals to a combined content of  $100 \mu\text{g g}^{-1}$  in any  
48 packaging material. Soda-lime glass is the most important type of glass used in packaging for food  
49 and beverages and is recycled at rates exceeding 90% in some European countries (7). However,  
50 historical recycling of certain products like cathode ray tubes and crystal glass have resulted in  
51 significant contamination of the cullet by (mainly) Pb (10). Given that metals in glass are considered  
52 to be inert, and rather than impede the expanded use of recycled glass in the production of  
53 packaging, a subsequent derogation of the  $100 \mu\text{g g}^{-1}$  limit was introduced (11). The derogation  
54 stipulated that heavy metals are not “intentionally” introduced during manufacturing and that an  
55 investigation be instigated should the regular production of glass from a given furnace exceed a  $200$   
56  $\mu\text{g g}^{-1}$  combined heavy metal concentration.

57 Despite these restrictions, there is very little published information on the heavy metal content of  
58 consumer container glass from which to make inferences about compliance and cullet  
59 contamination. Moreover, a recent article reporting high levels of Cd in enamels of glass bottles (12)

60 suggests that there exists the potential for increasing metal content of container glass in what is  
61 intended to be a closed loop system. The aims of this study were to determine the heavy metal  
62 content of contemporary container glass and decorative enamels by x-ray fluorescence (XRF)  
63 spectrometry. Alcoholic beverage bottles were targeted because they are widely available in a  
64 variety of different colours and many producers use enamels for logos, text, patterns or images.  
65 Selected samples were also subjected to a standard landfill leaching test in order to evaluate heavy  
66 metal mobilisation on disposal. Findings are discussed with respect to contamination of the soda-  
67 lime container glass recycle stream and potential impacts on human health and the environment.

68

## 69 **Experimental Section**

### 70 *Samples*

71 Bottled alcoholic products were purchased from local and national supermarkets between  
72 September 2017 and August 2018. Bottles contained a variety of drinks (beers, wines, spirits) of  
73 volume that ranged from 50 ml to 750 ml, and were either clear (including some that were frosted)  
74 or coloured green, ultraviolet-absorbing green (UVAG), or brown. Twenty four bottles,  
75 encompassing each glass colour type, were enamelled over part of the exterior surface with images,  
76 patterns, logos, text and/or barcodes of a single colour or multiple colours. In addition, unenamelled  
77 empty bottles and identifiable fragments ( $n = 68$ ) were sourced from the glass waste of a local  
78 establishment licensed to sell alcoholic drinks. For comparison, 12 clear, unenamelled drinking  
79 glasses constructed of more toughened glass and that are not generally recycled were sourced from  
80 local hardware stores and supermarkets.

### 81 *XRF analysis*

82 Samples were analysed for Pb, Cd, Cr and Hg and a range of other elements by portable, energy-  
83 dispersive x-ray fluorescence (XRF) spectrometry using a battery-operated Niton XLt3 950 He  
84 GOLDD+. Measurements were made in a shielded 4000 cm<sup>3</sup> laboratory accessory stand, with the  
85 instrument pointing nose-upwards and operated remotely by a laptop, where possible. For empty  
86 bottles too large to fit into the stand ( $n = 15$ ), the instrument was employed hand-held. Here,  
87 samples were cradled in a folded radiation protection apron on a stainless steel bench with  
88 measurements performed by placing the detector window vertically downward through the glass  
89 and activated using the trigger mechanism of the instrument. Measurements of the glass substrate  
90 were undertaken for 30 seconds in a consumer products-ceramics mode while measurements of  
91 enamelled areas were undertaken for 30 seconds in a plastics mode with a thickness correction of

92 0.05 mm applied. Where the enamelled area or colour to be probed was smaller than the 8-mm  
93 detector window, 3-mm collimation was applied by using the small-spot facility of the instrument;  
94 here, precise positioning was accomplished using video imagery generated by a CCD camera  
95 adjacent to the x-ray source in the detector window.

96 As a performance check, plastic discs containing known amounts of Pb, Cd, Cr and Hg (and ranging  
97 from about 100 to 1000  $\mu\text{g g}^{-1}$ ) were analysed several times during each measurement session, with  
98 the XRF returning values that were within 10% of known concentrations in all cases. In the accessory  
99 stand, method limits of detection for the ceramics mode were about 15, 10, 50, and 20  $\mu\text{g g}^{-1}$  for Pb,  
100 Cd, Cr and Hg, respectively, while detection limits in the plastics mode were about 30, 50, 100, and  
101 40  $\mu\text{g g}^{-1}$ , respectively. When the XRF was operated handheld, detection limits were approximately  
102 double the corresponding values achieved in the stand. Multiple measurements ( $n = 5$ ) performed  
103 on the same area of three samples positioned in the accessory stand revealed precisions in the  
104 ceramics mode of better than 10% and about 12% and 3% for Pb, Cd and Cr, respectively, and  
105 precisions in the plastics mode of better than 10% and about 5% and 10% (note that Hg was never  
106 detected). Hand-held, precision was lower but better than 15% in all cases where the metal was  
107 detected.

#### 108 *Leaching procedure and leachate analysis*

109 Fragments of glass from three decorated bottles and three undecorated bottles were subjected to  
110 the US Environmental Protection Agency Toxicity Characteristics Leaching Procedure (TCLP) (13, 14).  
111 The TCLP test is designed to mimic the fate of waste exposed to rainfall and other liquids percolating  
112 through landfill. Bottles were placed on a hard surface in individual jiffy bags and broken with a  
113 mallet. Between one and six fragments of < 1.5 cm in the longest dimension and up to 2.5 g in mass  
114 were carefully retrieved from each bag and weighed into a series of 50 ml screw-capped conical  
115 polypropylene centrifuge tubes. A solution of 0.1 M acetic acid, prepared from Fisher Scientific  
116 analytical grade glacial acetic acid in Elga Type 1 water (18.2 M $\Omega$ .cm), was added to each tube that  
117 resulted in a mass to volume ratio of 1:20, and the contents were then placed on a Grant-Bio PTR-60  
118 end-over-end shaker set at 30 rpm for 18 h at room temperature. Taking care not to disturb any  
119 glass fragments, 10 ml of each leachate were subsequently filtered through a 0.45  $\mu\text{m}$  Whatman  
120 filter directly into a series of 15 ml centrifuge tubes pending analysis. For a comparison, leachates  
121 arising from one decorated bottle that had a distinctive yellow precipitate or suspension were also  
122 transferred to 15 ml tubes without filtration.

123 Heavy metals in leachates were analysed by inductively coupled plasma mass spectrometry (ICP-MS)  
124 using a Thermo Scientific iCAP RQ with a concentric glass nebuliser and conical spray chamber. The

125 instrument was calibrated with matrix-matched mixed standards (up to 2 mg L<sup>-1</sup>) prepared by serial  
126 dilution of LabKings multi-element quality control solutions and was operated under conditions  
127 described elsewhere (15).

128

## 129 **Results**

130 Descriptive statistics summarising the concentrations of Pb, Cd and total Cr in the glass substrates of  
131 the samples are shown in Table 1 (as above, Hg was never detected). Thus, out of 89 bottles and  
132 fragments analysed, 76 were positive for Pb, with the relative frequency of detection lower in clear  
133 glass than in other colours and, overall, concentrations ranging from < 30 µg g<sup>-1</sup> to over 1120 µg g<sup>-1</sup>.  
134 The highest mean concentration was encountered in green glass and one-way ANOVA performed in  
135 Minitab v17 revealed that concentrations in this colour were significantly higher ( $p < 0.05$ ) than  
136 those in clear or brown glass. Cadmium was detected in all colours of glass at concentrations that  
137 were relatively invariant and ranging from about 11 to 35 µg g<sup>-1</sup>; according to one-way ANOVA,  
138 mean concentrations were statistically indistinguishable among the colour types. Chromium was  
139 detected in all green and UVAG bottles with mean concentrations of about 2000 and 700 µg g<sup>-1</sup>,  
140 respectively, but was only detected in 40% of brown glass and was never detected in clear glass.  
141 Among additional elements analysed by the XRF, Bi, Ni, Sb, Sn and Zr were present in at least three  
142 bottles from each colour category, Zn was encountered in most green, UVAG, and brown samples  
143 but never detected in clear glass, Cu was only detected among brown samples, Fe was present  
144 across all colour categories but concentrations were significantly lower ( $p < 0.05$ ) in clear glass, and  
145 As, Se and Sn were never detected. By contrast, among the 12 clear drinking glasses analysed, Pb  
146 was detected twice, Cr once and Fe and Sb were detected in three cases each.

147 The characteristics of the enamelled bottles are shown in Table 2, along with mean concentrations  
148 of Pb, Cd and Cr returned by the XRF for each enamelled colour probed (as above, Hg was never  
149 detected). Here, bottle colours are defined as in Table 1, the place of origin is as indicated on the  
150 bottle (which may refer to the beverage or bottling and not necessarily the glass bottle or enamel),  
151 and the surface area occupied by enamel represents a best estimate from visual inspection relative  
152 to the surface area of the whole product (excluding the base) and includes all enamel colours. Figure  
153 1 illustrates a part-enamelled bottle of wine that was analysed along with resulting XRF spectra and  
154 metal concentrations at two locations.

155 Lead was detected at concentrations of tens of thousands of µg g<sup>-1</sup> on various colours of enamels on  
156 five bottles of wine whose glass colours were green, UVAG, and clear, and on white enamel of a

157 brown bottle of beer, but was only detected elsewhere at levels below  $150 \mu\text{g g}^{-1}$  and more typical of  
158 the glass substrate itself. Cadmium was returned at concentrations ranging from about 1000 to  
159 20,000  $\mu\text{g g}^{-1}$  on many of these enamels, as well as the red, white and yellow enamels from a clear  
160 bottle of spirits and the yellow, red or orange enamels of an additional clear bottle of wine, two  
161 brown bottle of cider and two brown bottles of beer. Total Cr was detected in enamels from a  
162 number of bottles most of which were clear and at concentrations ranging from about 30 to 1700  $\mu\text{g}$   
163  $\text{g}^{-1}$ , suggesting that the metal was a component of the enamel and not the underlying glass. Overall,  
164 it appears that the enamels of twelve products out of 24 tested are based wholly or partly on  
165 compounds of either or both Pb and Cd, with the former restricted to wine bottles and a bottle of  
166 beer and the latter distributed across a broader range of beverage containers.

167 Concentrations of Cd and Pb in the glass leachates are shown in Table 3 (note that Cr was not  
168 detected). Cadmium concentrations in filtered leachates are  $< 1 \mu\text{g L}^{-1}$  for undecorated glass  
169 fragments and range from about 11 to 3200  $\mu\text{g L}^{-1}$  for fragments whose exterior surfaces were partly  
170 decorated, with variation among fragments from the same bottle presumably reflecting different  
171 degrees and colours of décor across the glass surface. By comparison, concentrations of Cd in the  
172 three unfiltered leachates arising from a bottle decorated with yellow enamel and where a  
173 suspension or precipitate was evident exceed  $8000 \mu\text{g L}^{-1}$ , suggesting that in some cases, the metal  
174 may be mobilised or precipitated into a fine particulate form. Lead concentrations in leachates are  $<$   
175  $1 \mu\text{g L}^{-1}$  for undecorated glass fragments, between about 4 and  $10 \mu\text{g L}^{-1}$  for decorated fragments  
176 rich in Cd but where XRF failed to detect Pb, and between 50 and  $1240 \mu\text{g L}^{-1}$  for fragments where Pb  
177 was a distinct component of the décor.

178

## 179 Discussion

180 Both Pb and Cd appear to be widely distributed at relatively low levels in contemporary soda glass  
181 used to store alcoholic drinks; while total Cr was detected in many samples, it is likely to be present  
182 as chromic oxide, with or without iron oxide, for colour rather than as compounds of the more toxic  
183 Cr(VI). Concentrations of Pb reported here are consistent with values reported for six 750 ml  
184 commercial bottles of different colour and sourced in the EU that were tested just after the  
185 introduction of the original Packaging and Packaging Waste Directive (median =  $179 \mu\text{g g}^{-1}$ ; range =  
186  $93$  to  $1900 \mu\text{g g}^{-1}$ ; 10). This suggests that over the past two decades the glass cullet has remained  
187 broadly similar in respect of Pb, reflecting the historical and contemporary contamination by Pb-  
188 bearing glass (for instance, from cathode ray tubes, fluorescent light bulbs, old wine capsules, and  
189 leaded crystal articles). In contrast, however, Cd was never detected in these six samples ( $< 1 \mu\text{g g}^{-1}$ ),

190 suggesting that the Cd content of the cullet may have increased over time through the improper use  
191 or disposal of Cd-based products.

192 The original Packaging and Packaging Waste Directive laid out a gradual reduction in the limit of  
193 combined concentrations of Pb, Cd, Cr(VI) and Hg in glass that, after 2001, was to be set at  $100 \mu\text{g g}^{-1}$   
194 (9). On this basis, and using summed concentrations of Pb and Cd, non-compliance would occur in  
195 about one half ( $n = 42$ ) of the glass samples analysed in the present study. In one case, the original  
196 directive limit of  $600 \mu\text{g g}^{-1}$  would be exceeded solely due to the presence of Pb. However,  
197 recognising that the necessary reduction in Pb content would entail a significant and undesired  
198 reduction in glass recycling rate, a derogation to the directive in respect of heavy metals was  
199 introduced in 2001 with a  $200 \mu\text{g g}^{-1}$  long-term concentration limit for any individual glass furnace  
200 (11). This derogation expired in 2006 but a subsequent notification has prolonged it indefinitely (16).

201 From a health perspective, container glass contaminated with Pb and Cd at such concentrations is  
202 unlikely to pose a significant risk to the consumer. This is because the metals are incorporated into  
203 the glass matrix and are very insoluble. For instance, Guadagnino and Dall'Igna (10) demonstrated  
204 that the maximum amount of Pb released by a standard 4% acetic acid test was  $9 \mu\text{g L}^{-1}$  for a bottle  
205 whose Pb content in the glass was  $1900 \mu\text{g g}^{-1}$ , and in the present study, Cd and Pb concentrations in  
206 filtered 0.1 M acetic acid leachates from unenamelled glass fragments were  $< 1 \mu\text{g L}^{-1}$ . These  
207 concentrations compare with drinking water standards of  $10 \mu\text{g L}^{-1}$  and  $5 \mu\text{g L}^{-1}$  for Pb and Cd,  
208 respectively, defined by the UK Drinking Water Inspectorate (17) and recommended by the World  
209 Health Organisation (18).

210 The decorated enamels of half of bottles tested were found to contain high concentrations of Pb  
211 and/or Cd. The former metal as an oxide has been employed as a component of the flux to reduce  
212 the firing temperature of the enamel (19) while compounds of the latter metal are often used as  
213 heat stable and brightly coloured pigments (20). The association of Cd with Se in many cases (and in  
214 an average mass ratio of about 10:1) is consistent with the use of Cd sulphoselenide pigments, but  
215 its wider occurrence without Se on many neutrally coloured enamels implies an additional or  
216 alternative use. It appears that CdO can also serve as a flux in some applications (21) and it is  
217 possible, therefore, that this compound is employed in enamelled decorations on container glass,  
218 and either with or without PbO. As with the glass substrate itself, and despite higher concentrations  
219 of toxic metals, enamels are unlikely to pose a direct, significant human health threat as decorations  
220 are externally embossed and do not extend to the neck area where contact with the mouth could  
221 occur should the contents be consumed directly from the bottle.



222 Although not an immediate or direct threat to human health, the use of toxic metals in the  
223 enamelling of glass bottles that are otherwise in a closed recycling loop is predicted to result in a  
224 progressive increase in the metal content of the glass cullet or an increase in waste metal emitted by  
225 glass furnace facilities. The significance the two routes depends on the quantity of bottles  
226 enamelled, the concentrations of Pb and Cd in enamels relative to the corresponding concentrations  
227 in the glass substrates, and the volatilisation points of the components of the enamels and any  
228 decomposition products relative to the melting point of glass.

229 Mass balance considerations suggest that contamination from enamel components is likely to be  
230 more significant for Cd than Pb because (i) “baseline” concentrations of the latter are considerably  
231 higher in the glass substrate through improper or historical recycling of leaded-products, and (ii) Cd  
232 appears to be more widely used in the enamelling of contemporary bottles. An upper estimate of  
233 the propensity for Cd contamination of the glass cullet may be calculated from representative  
234 dimensions and characteristics of enamel and glass substrate. Thus, an enamel of 0.05 mm in  
235 thickness and containing  $10,000 \mu\text{g g}^{-1}$  of Cd that covers 15% of the glass surface (including the base)  
236 whose average thickness is 3 mm is equivalent to a net concentration of  $25 \mu\text{g g}^{-1}$  Cd in the product;  
237 that is, one Cd-enamelled bottle in every 25 bottles of equal size would result in an increase in the  
238 Cd content of the cullet of  $1 \mu\text{g g}^{-1}$  for every recycling process undertaken. Observations of the  
239 present study suggest that half of enamelled bottles contain Cd in the décor but the percentage of  
240 commercial bottles on the market or recycled that is enamelled is unknown.

241 The proportion of a heavy metal used in enamelling that is lost to the environment may be  
242 evaluated from thermodynamic considerations and experimental studies. For Pb, the boiling points  
243 of the metal ( $1749 \text{ }^\circ\text{C}$ ) and its monoxide ( $1472 \text{ }^\circ\text{C}$ ) are greater than the temperature at which post-  
244 consumer glass is melted ( $1350$  to  $1400 \text{ }^\circ\text{C}$ ; 7), and empirical evidence suggests that it is largely  
245 retained in the recyclate (22, 23). For Cd, the case is more complex as the boiling points of the metal  
246 and monoxide are  $767 \text{ }^\circ\text{C}$  and  $1559 \text{ }^\circ\text{C}$ , respectively, while the sulphide (used to pigment enamels)  
247 sublimes at  $980 \text{ }^\circ\text{C}$ . Ross (24) suggests that a significant proportion of metals like Cd may not remain  
248 in the glass being melted but may be emitted through the stack or condense within the exhaust  
249 system. Accumulation in refractory lining and flue debris is a concern for worker exposure during  
250 cleaning, demolition or waste disposal.

251 Regardless of the fate of Pb and Cd in the recycling process, it is unclear whether enamelling of  
252 consumer glass bottles with these metals complies with relevant packaging laws. The UK Packaging  
253 Regulations, set out as Statutory Instrument 1640 (25) and based on EU Directive 94/62/EC (9) states  
254 that no regulated heavy metals must be intentionally introduced during the manufacture of glass

255 packaging or components. However, a subsequent guidance document (26) refers to an Annex  
256 regarding “some known uses” of heavy metals in packaging and this includes enamels to decorate  
257 bottles. Here, it states that Pb may be encountered as a basic component of enamels while Cd could  
258 be found in bright yellow and red colours. The document also states that (i) metals will occur in small  
259 levels in most cases, (ii) some level of compliance monitoring should be performed, and (iii) a  
260 number of major producers signed a voluntary agreement aiming to phase out heavy metals in  
261 enamels.

262 Clearly, enamels are added intentionally and for appearance, and Pb and Cd concentrations in  
263 enamels are not “small” (on the order of tens of thousands of  $\mu\text{g g}^{-1}$ ). Precise metal concentrations  
264 in enamelled glass products are dependent on the coverage of the decorated surface and its  
265 thickness relative to the underlying glass, with net concentrations varying considerably across the  
266 decorated product. Significantly, the results of the present study reveal that Cd is not restricted to  
267 brightly coloured yellows and reds but a range of other colours, suggesting that the metal may also  
268 be a constituent of the flux. Results also show that Cd is often used without a Pb-based flux and that  
269 many brightly coloured enamels use neither Pb nor Cd.

270 The Model Toxics in Packaging Legislation, adopted by nineteen US states (27) prohibits the  
271 intentional introduction of metals “where its continued presence is desired in the final package or  
272 packaging component to provide a specific characteristic, appearance, or quality” and includes inks  
273 and labels under “packaging component”. Exemptions may apply where there are no feasible  
274 alternatives and, with respect to glass and ceramics, vitrified labels provided that Cd and Pb do not  
275 leach more than  $1000 \mu\text{g L}^{-1}$  and  $5000 \mu\text{g L}^{-1}$ , respectively, according to the US EPA TCLP (13). Clearly,  
276 however, enamels are not chemically inert under conditions simulating liquid percolation through a  
277 landfill, with the present study showing exceedance of the Cd limit for various enamelled glass  
278 fragments and considerable exceedance if leachates suspensions or precipitates are not filtered. By  
279 definition, therefore, fragments of such products are deemed as “toxic” or “hazardous” waste.

280 Given safer decorative alternatives are available that engender the same effect to the product (28),  
281 questions arise as to why toxic metals are still employed and where they are sourced from,  
282 especially since a voluntary phase out is indicated in by the UK Department for Business, Innovation  
283 and Skills (26) and that a general precautionary principle to such metals is recommended (29). To  
284 this end, suppliers contacted by the author indicated that for drinks produced in the UK, pre-  
285 enamelled bottles are outsourced from abroad (but including countries within the EU), while for  
286 imported products bottles are manufactured by companies that may or may not be located in the  
287 same country as that producing the beverage.

288 In summary, high concentrations of Pb and Cd are commonly encountered in the decorative enamels  
289 of contemporary glass bottles. While not an immediate risk to the consumer through beverage  
290 consumption or the handling or storage of bottles, the pervasive use of these heavy metals in what  
291 is largely a closed loop have potentially more serious impacts on the environment and the health of  
292 workers employed in the glass recycling industry.

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374 Table 1: Number of cases in which Pb, Cd and Cr were detected in container glass of different  
 375 colours and in clear drinking glasses, along with summary statistics for resulting concentrations.

		Pb, $\mu\text{g g}^{-1}$	Cd, $\mu\text{g g}^{-1}$	Cr, $\mu\text{g g}^{-1}$
brown ( $n = 23$ )	<i>n</i>	22	19	9
	mean	51.2	20.5	133
	median	45.9	22.3	132
	sd	17.0	6.9	64.0
	min	28.1	11.3	32.0
	max	95.2	35.2	259
green ( $n = 20$ )	<i>n</i>	20	10	20
	mean	202	21.7	2020
	median	154	20.0	2030
	sd	222	5.4	488
	min	82.6	14.4	800
	max	1120	30.0	3000
clear ( $n = 28$ )	<i>n</i>	18	16	0
	mean	73.3	18.3	
	median	66.9	17.2	
	sd	23.1	4.7	
	min	35.1	11.7	
	max	123	27.9	
UVAG ( $n = 18$ )	<i>n</i>	16	10	18
	mean	161	22	700
	median	154	20	632
	sd	46.3	5.2	389
	min	28.2	14.1	155
	max	235	31.5	1790
drinking glasses ( $n = 12$ )	<i>n</i>	2	0	1
	mean	45.7		22.2
	median			
	sd			
	min	13.6		
	max	77.7		

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383 Table 2: Details of the enamelled bottles analysed in the study and concentrations of Pb, Cd and Cr,  
 384 in decorated areas defined by colour. Asterisks denote bottles used for the leaching test.

sample no.	drink	bottle colour	volume, ml	place of origin	estimated enamelled		Pb, µg g <sup>-1</sup>	Cd, µg g <sup>-1</sup>	Cr, µg g <sup>-1</sup>
					surface, %	colours			
1	flavoured vodka	clear	700	Sweden	35	green orange pink red			
2*	advocaat	clear	700	Netherlands	25	red white black		4330 1850	904
3	flavoured vodka	clear	50	France	20	yellow white red			
4	gin	clear	700	UK	90	black red			
5	limoncello	clear	500	Italy	7	green			1720
6	flavoured vodka	clear	50	France	20	yellow			
7	white wine	UVAG	750	Australia	20	white green black	76,200 70,200 46,500	9,980 10,400	410 1710
8*	white wine	green	750	Chile	5	beige purple	1,360 27,400	4540	
9	white wine	clear	750	Chile	10	green turquoise cream	10,100 105,000 20,300	2300 16,300	2800
10	red wine	UVAG	750	Chile	5	blue cream			
11	red wine	UVAG	750	Australia	10	red white	46,500 10,900	19,400 1170	
12	white wine	clear	750	Germany	3	white			
13	white wine	clear	750	Chile	30	orange yellow green white		5960	290
14	sparkling white wine	clear	750	Spain	10	white	19,300	1630	582
15	sparkling rose wine	clear	750	South Africa	5	white			
16	beer	clear	330	Mexico	35	blue			
17	beer	brown	330	Belgium	7	white			1090
18	beer	clear	570	Mexico	25	white blue			
19	beer	brown	330	UK	20	yellow white		6990	
20	beer	brown	330	UK	20	orange white	93.4 143	6640	32.4 57.1 67.9
21	beer	brown	330	Belgium	7	white	62.5		
22	beer	brown	660	UK	10	white	36,200	3420	
23*	cider	brown	330	South Africa	30	yellow		6060	
24	cider	brown	330	South Africa	30	red		4760	

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393 Table 3: Concentrations of Pb and Cd in leachate arising from glass fragments of different enamelled  
 394 and unenamelled bottles. Data in parentheses denote concentrations in unfiltered leachates.

sample no.	bottle colour	enamelled colour/s	Pb, $\mu\text{g L}^{-1}$	Cd, $\mu\text{g L}^{-1}$
2	clear	red/black	6.7	292
		red/white	1.7	656
		red/white	7.4	665
8	green	beige	51.2	10.7
		purple/beige	317	53.1
		purple/beige	1240	184
		purple/beige	191	34.1
		purple	1120	163
23	brown	yellow	4.1 (4.2)	2330 (8620)
		yellow	3.9 (4.1)	2170 (9860)
		yellow	5.8 (5.8)	3230 (11,600)
30	UVAG	unenamelled	0.9	0.5
48	green	unenamelled	0.8	<0.1
68	brown	unenamelled	0.3	0.6

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Figure 1: A UVAG-coloured and enamelled wine bottle with spectra arising from the XRF measurements (handheld and 3-mm collimation) of the red and white decorated areas indicated by yellow circles. Note the presence of Se in the red enamelled area indicative of the use of cadmium sulphoselenide. Also shown are Cd, Pb and Cr concentrations ( $\pm 2$  counting errors) over both measurement areas.



