2019-07-16

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http://hdl.handle.net/10026.1/14646

10.1021/acs.est.9b01726
Environmental Science and Technology
American Chemical Society

Heavy metals in the glass and enamels of consumer container bottles

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Accepted 11th June 2019

DOI: 10.1021/acs.est.9b01726

Embargoed until June 11th 2020

Abstract

The glass and enamelled decorations of bottles of alcoholic beverages sourced from retailers in the UK were analysed by x-ray fluorescence spectrometry for various heavy metals. In the glass substrate, lead, cadmium and chromium were present at concentrations up to about 1100 μg g^{-1}, 1100 μg g^{-1} and 3000 μg g^{-1}, respectively, but their environmental and health risks are deemed to be low significance. Of more concern from an environmental and, potentially, occupational exposure perspective are the concentrations and mobilities of Pb and Cd in the enamels of many bottles. Thus, Pb concentrations up to about 100,000 μg g^{-1} were found on the décor of various wine bottles and a beer bottle, and Cd concentrations of up to 20,000 μg g^{-1} were measured in the decorated regions on a range of spirits, beer and wine bottles. Moreover, maximum concentrations that leached from enamelled glass fragments according to a standard test that simulates water and other liquids percolating through a landfill were about 1200 and 3200 μg L^{-1} for Pb and Cd, respectively, with several fragments exceeding the US Model Toxins in Packaging Legislation and, therefore, defined as "hazardous". Given that safer decorative alternatives are available and that a precautionary principle should be adopted for toxic heavy metals, the pervasive use of Pb and Cd in the enamels of consumer bottles is brought into question.

Introduction

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

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

Despite these restrictions, there is very little published information on the heavy metal content of consumer container glass from which to make inferences about compliance and cullet contamination. Moreover, a recent article reporting high levels of Cd in enamels of glass bottles (*12*) suggests that there exists the potential for increasing metal content of container glass in what is intended to be a closed loop system. The aims of this study were to determine the heavy metal content of contemporary container glass and decorative enamels by x-ray fluorescence (XRF) spectrometry. Alcoholic beverage bottles were targeted because they are widely available in a variety of different colours and many producers use enamels for logos, text, patterns or images. Selected samples were also subjected to a standard landfill leaching test in order to evaluate heavy metal mobilisation on disposal. Findings are discussed with respect to contamination of the soda-lime container glass recyclate stream and potential impacts on human health and the environment.

Experimental Section

Samples

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

XRF analysis

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

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

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

Leaching procedure and leachate analysis

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

Heavy metals in leachates were analysed by inductively coupled plasma mass spectrometry (ICP-MS) using a Thermo Scientific iCAP RQ with a concentric glass nebuliser and conical spray chamber. The instrument was calibrated with matrix-matched mixed standards (up to 2 mg L^{-1}) prepared by serial dilution of LabKings multi-element quality control solutions and was operated under conditions described elsewhere (*15*).

Results

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

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

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

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

Discussion

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

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

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

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

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

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

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

Regardless of the fate of Pb and Cd in the recycling process, it is unclear whether enamelling of consumer glass bottles with these metals complies with relevant packaging laws. The UK Packaging Regulations, set out as Statutory Instrument 1640 (*25*) and based on EU Directive 94/62/EC (*9*) states that no regulated heavy metals must be intentionally introduced during the manufacture of glass packaging or components. However, a subsequent guidance document (*26*) refers to an Annex regarding "some known uses" of heavy metals in packaging and this includes enamels to decorate bottles. Here, it states that Pb may be encountered as a basic component of enamels while Cd could be found in bright yellow and red colours. The document also states that (i) metals will occur in small levels in most cases, (ii) some level of compliance monitoring should be performed, and (iii) a number of major producers signed a voluntary agreement aiming to phase out heavy metals in enamels.

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

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

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

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

Acknowledgements

Dr Andrew Fisher, UoP, is thanked for analysing the leachate samples. The study was part-funded by a Plymouth Marine Institute HEIF grant.

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

		Pb, μg g^{-1}	Cd, μg g^{-1}	Cr, μg g^{-1}
brown (*n* = 23)	*n*	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)	*n*	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)	*n*	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)	*n*	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)	*n*	2	0	1
	mean	45.7		22.2
	median			
	sd			
	min	13.6		
	max	77.7		

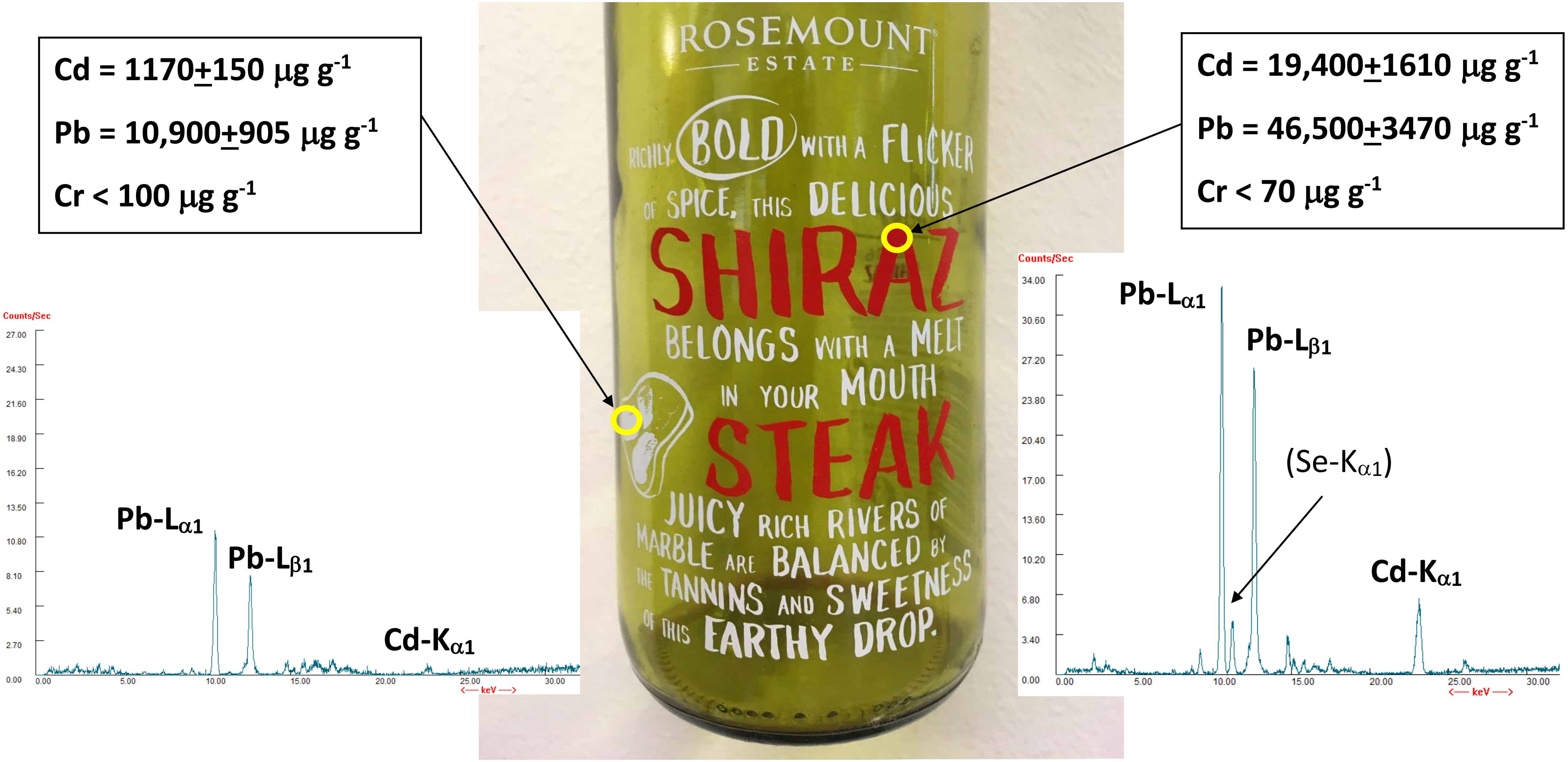
Table 2: Details of the enamelled bottles analysed in the study and concentrations of Pb, Cd and Cr, in decorated areas defined by colour. Asterisks denote bottles used for the leaching test.

sample no.	drink	bottle colour	volume, ml	place of origin	estimated enamelled surface, %	enamelled colours	Pb, μg g^{-1}	Cd, μg g^{-1}	Cr, μg g^{-1}
1	flavoured vodka	clear	700	Sweden	35	green			
						orange			
						pink			
						red			
2*	advocaat	clear	700	Netherlands	25	red		4330	
						white		1850	
						black			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	76,200	9,980	
						green	70,200	10,400	410
						black	46,500		1710
8*	white wine	green	750	Chile	5	beige	1,360		
						purple	27,400	4540	
9	white wine	clear	750	Chile	10	green	10,100	2300	
						turquoise	105,000	16,300	2800
						cream	20,300	2760	
10	red wine	UVAG	750	Chile	5	blue			
						cream			
11	red wine	UVAG	750	Australia	10	red	46,500	19,400	
						white	10,900	1170	
12	white wine	clear	750	Germany	3	white			
13	white wine	clear	750	Chile	30	orange			
						yellow		5960	
						green			290
						white			
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		6990	
						white	93.4		32.4
20	beer	brown	330	UK	20	orange	143	6640	57.1
						white			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	

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

sample no.	bottle colour	enamelled colour/s	Pb, μg L^{-1}	Cd, μg 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

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 (± 2 counting erors) over both measurement areas.



Cd = 1170±150 μg g^{-1}

Pb = 10,900±905 μg g^{-1}

Cr < 100 μg g^{-1}

Cd = 19,400±1610 μg g^{-1}

Pb = 46,500±3470 μg g^{-1}

Cr < 70 μg g^{-1}