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High levels of migratable lead and cadmium on decorated drinking glassware

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Abstract

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

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

1. Introduction

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

Among food contact materials, ceramicware has been the focus of much attention over the past few decades because of the use of various heavy metals and metalloids in its finishing (Ajmal et al., 1997; Sheets et al., 1999; Henden et al., 2011; Dong et al., 2015). Here, the glaze usually consists of a frit-clay suspension combined with a metallic oxide flux that reduces the softening temperature of the various components, while decorative enamel or metal (e.g. gold leaf) may be applied either before firing (underglaze) or on top of the glaze before re-firing at a lower temperature. Being a powerful flux and an effective solvent for other glaze components, coupled with a wide processing latitude, PbO remains a favourable component of ceramicware glaze, despite lead-free replacements having been developed (Beldì et al., 2016). Regarding decoration, colour pigments are limited to those that are thermally stable during firing, with a greater range available for lower temperature overglazing. Popular pigments yielding brilliant colours include chrome oxide (green), zirconium vanadium blue and cadmium sulphoselenides (red) (Lehman, 2002).

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

Externally decorated glass hollow-ware intended for beverages is generally overglazed, with a migratability test and maximum limits adopted voluntarily by the glass industry that are limited to the area within 20 mm of the rim and where direct contact with the lips occurs (ASTM, 2009). Despite the availability of such a test, coupled with well-publicised recalls of decorated glasses intended for children because of the presence of Cd-based paint (Mead, 2010), there has been no systematic investigation into the nature of the decorative materials employed by the industry and the potential for consumer exposure to hazardous elements. To the author’s knowledge, the only published scientific study in this respect compared the migration of Pb and Cd from the lip areas of decorated, food-contact ceramicware and glassware available on the Polish market (Rebeniak et al., 2014); thus, while most ceramicware was compliant, with the metals undetected in many cases, about 20% of glassware tested (n = 393) was non-compliant with respect to national regulations.

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

2. Materials and methods

2.1. Sampling and sample categorisation

Excluding replicates, a total of 72 glass products used to drink from directly and that had been enamel-decorated on part of the exterior were considered in the present study. New glassware was purchased in April and May 2017 from local supermarkets (n = 10), homeware stores (n = 11) and gift shops (n = 17), while older items were purchased from second-hand (charity) shops (n = 15) or were borrowed from colleagues but originally purchased in the UK (n = 19). Samples were categorised according to type or function as highball (n = 15), lowball (n = 8), mug (n = 3), beer (n = 16), shot (n = 21), wine-cocktail (n = 4) or jar (n = 5), with items in the latter category characterised by distinctly thicker (soda-lime) glass and a screw-cap lid. Individual products were photographed and the internal volume, minimum distance of decorative enamel to the rim and dominant colours of application recorded. The estimated coverage of the external surface that was decorated (as a percentage and excluding the base) and, where stated, country of manufacture were also noted.

2.2. Sample analysis

Samples were analysed by portable XRF spectrometry using a Niton XL3t 950 He GOLDD+ for a suite of elements, of which Pb and Cd as hazardous and/or restricted metals are the focus of the present study. Where possible, samples were contained by a 4000 cm^3 Thermo Fisher Scientific accessory test stand (PN 420-017) with the XRF securely fitted nose-upwards to the baseplate of the stand and operated remotely from a laptop. For glassware too large to be contained by or repositioned within the test stand, analyses were performed handheld and on a stainless steel table, cushioning the samples on a folded lead apron and securing them between a number of suitably solid and attenuating objects.

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

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

2.3. Quality assurance

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

The performance of the XRF in the plastics mode and with 3-mm collimation was verified by the regular analysis of 13-mm thick Niton polyethylene discs impregnated with Pb and Cd (PN 180-554, batch SN PE-071-N; PN 180-619, LOT#T-18), with mean measured concentrations returned that were always within 10% of mean certified values. As an additional measure of instrument performance on thin layers, six standard reference paint films certified for Pb concentrations on an areal basis (SRM 2570 to 2575; National Institute of Standards & Technology) and uniformly coloured enamelled surfaces of selected glassware samples were analysed at the same locations using both the plastics mode and a lead paint mode (the latter operating at 50 kV and 40 μA and without collimation). Concentrations of Pb in the reference films returned in μg cm^{-2} using the lead paint mode were within 10% of corresponding certified values and were highly correlated with concentrations returned in the plastics mode on a weight basis (n = 6; r = 0.980), with a slope, derived from linear regression analysis, of 40.0 cm^2 g^{-1} and that was valid to a Pb concentration of at least 150,000 μg g^{-1} on a weight basis. Concentrations of Pb returned by both modes on the enamelled sample surfaces were also highly correlated (n = 18; r = 0.926) with a slope (= 40.7 cm^2 g^{-1}) that was almost identical to that defining the relationship in the reference paint films.

2.4. Extraction tests

To evaluate the migratability of Pb and Cd from the externally enamelled surfaces of drinking glassware, 14 items of varying source, type and colour whose metal-positive décor extended to the lip area were subject to the ASTM (2009) standard extraction test, with a shot glass decorated with Pb- and Cd-free enamelling serving as a control. Thus, interior volumes to 6 mm from the rim were determined by addition of tap water from a measuring cylinder before glassware was cleaned in detergent, rinsed with distilled water and air-dried. Each sample was then marked on the exterior substrate at the 20 mm level and placed, inverted, into an acid-cleaned 300 ml Pyrex crystallisation dish or, for the largest items or those with handles, an acid-cleaned 1 L Pyrex beaker. A solution of 4% glacial acetic acid (Fisher Scientific analytical grade) at pH 2.6 was carefully added to each container from a polyethylene measuring cylinder to the 20 mm mark on the sample exterior and the volume recorded. After extraction for 24 h at room temperature and in the dark, 15 ml of acetic acid was pipetted from each dish or beaker into a series of 50 ml screw-capped polypropylene centrifuge tubes that were stored in a refrigerator at 4 ^{o}C pending analysis. Five further samples, including duplicates of three products extracted in acetic acid, were also extracted in a less aggressive carbonated beverage (Coca Cola Classic; pH = 2.6) for 24 h and at room temperature using an otherwise identical protocol, with centrifuge tubes stored likewise pending analysis. Meanwhile, enamelled surfaces of the glassware subject to extraction were air-dried for 24 h before being examined for physical modification and colour change and reanalysed by XRF as above.

Acetic acid and Coca Cola extracts were analysed for Pb (220.353 nm) and Cd (228.802 nm) by ICP-optical emission spectrometry using a Thermoscientific iCAP 7400. The instrument was calibrated using four mixed standards and a blank prepared by serial dilution of LabKings standard solutions (Hilversum, NL) in 2% HNO_3, with settings as follows: exposure time = 2 s; RF power = 1150 W; nebuliser, coolant and auxiliary gas flows = 0.50, 12 and 0.5 L min^{-1}, respectively; viewing height = 12 mm; uptake time = 50 s; wash time = 15 s. Limits of detection, based on three standard deviations about multiple measurements of blanks, were about 0.01 mg L^{-1} for both metals

3. Results

3.1. Sample characteristics

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

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

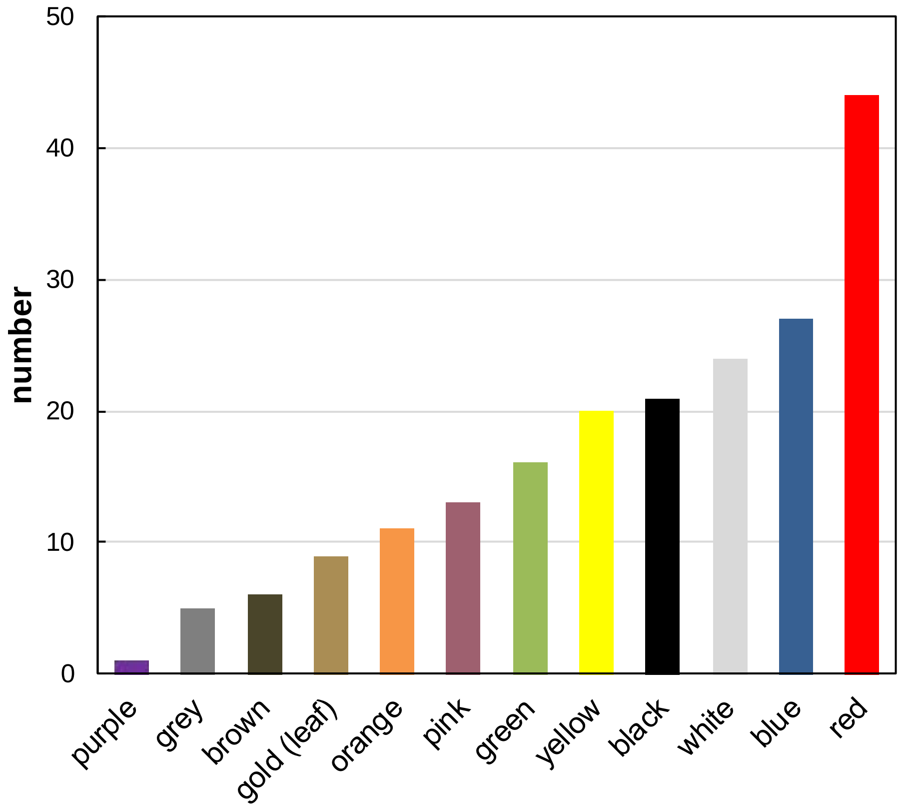


Figure 1: Frequency distribution of the colours analysed on the decorated glassware.

3.2. Pb and Cd concentrations in decorative enamel

The concentrations of Pb and Cd on a dry weight basis arising from the analyses of all decorated surfaces by XRF in the plastics mode analysed are summarised in Table 1, with the spatial and colour distribution of elemental concentrations on the exterior of a supermarket lowball tumbler exemplified in Figure 2. Overall, Pb was detected on 139 decorated surfaces, or about 70% of those analysed, with concentrations spanning five orders of magnitude (40 μg g^{-1} to about 40% by weight) and a median concentration of about 60,000 μg g^{-1}. (On an areal basis, the range and median are equivalent to about 1 to 10,000 μg cm^{-2} and 1500 μg cm^{-2}, respectively.) The metal was detected in all sample categories with the exception of jars and across all colours recorded (including the decorative gold leaf of some items), with 52 products out of a total of 72 containing at least one colour that was Pb-positive. Items associated with the surfaces containing Pb concentrations exceeding 10% by weight were sourced both new and second-hand; however, of these, only two supermarket highball glasses bearing red patterns and a gift store highball glass decorated with a cartoon were labelled with the country of manufacture (and as Turkey, France and China, respectively).

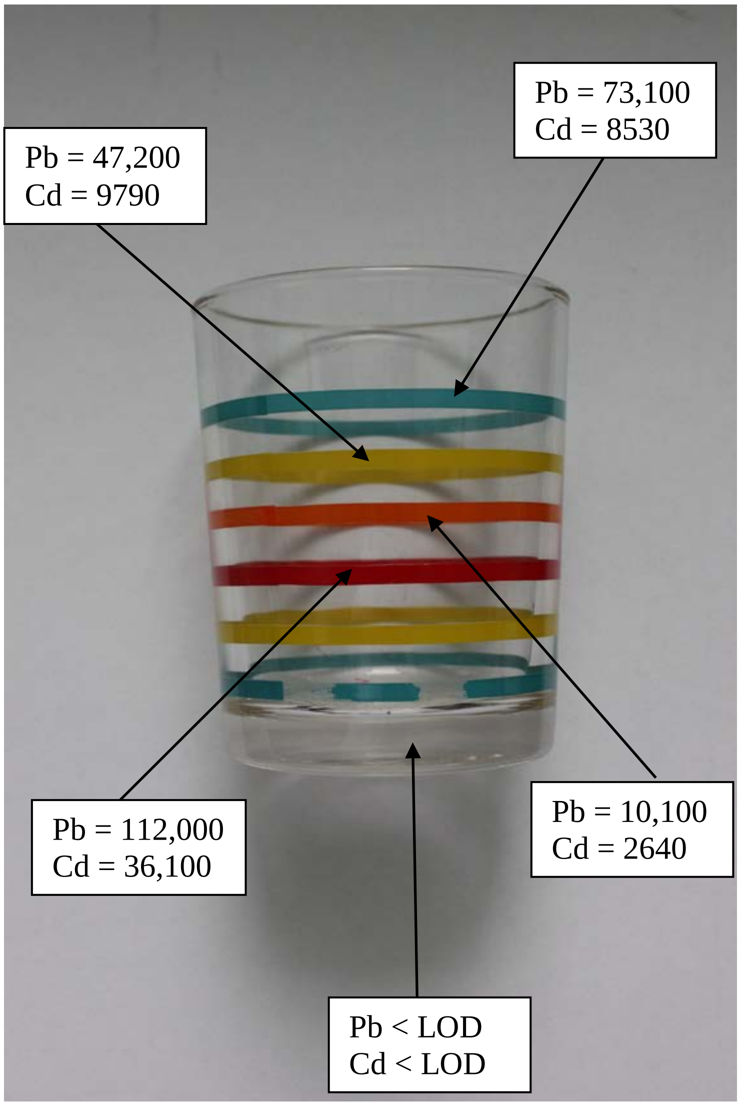


Figure 2: The distribution of Pb and Cd concentrations (in $\mu g\ g^{-1}$) on the exterior of a lowball tumbler purchased from a supermarket. Note the deterioration of the lowest (blue) ring, evident at the time of purchase.

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

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

	< 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

Other potentially hazardous elements detected in glassware by XRF but not considered in the present study included As, Cr, Sb and Se. Thus, once spectral overlap from Pb had been accounted for (Pb-Lα = 10.55 keV; As-Kα = 10.54 keV), As was encountered in 20 cases and at concentrations up to 100 $\mu g\ g^{-1}$. The presence of similar concentrations of As in the underlying vitreous substrate, however, is consistent with the occurrence of residual arsenic acid employed as an intermediate fining agent in the manufacture of the glass itself. Chromium concentrations in the decorated surfaces spanned three orders of magnitude and with a maximum concentration of about 20,000 μg g^{-1}. Positive results were encountered on 41 items and the metal exhibited a distinct bias towards dark, achromatic paints; specifically, all but one grey and > 90% of black formulations contained Cr, with nine out of the twelve highest measured concentrations of the metal encountered in the latter colour. Although Cr was associated with Pb in 74 analyses, the two metals were not significantly correlated, either overall or on an individual colour basis.

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

3.2. Extraction of Pb and Cd from decorated surfaces

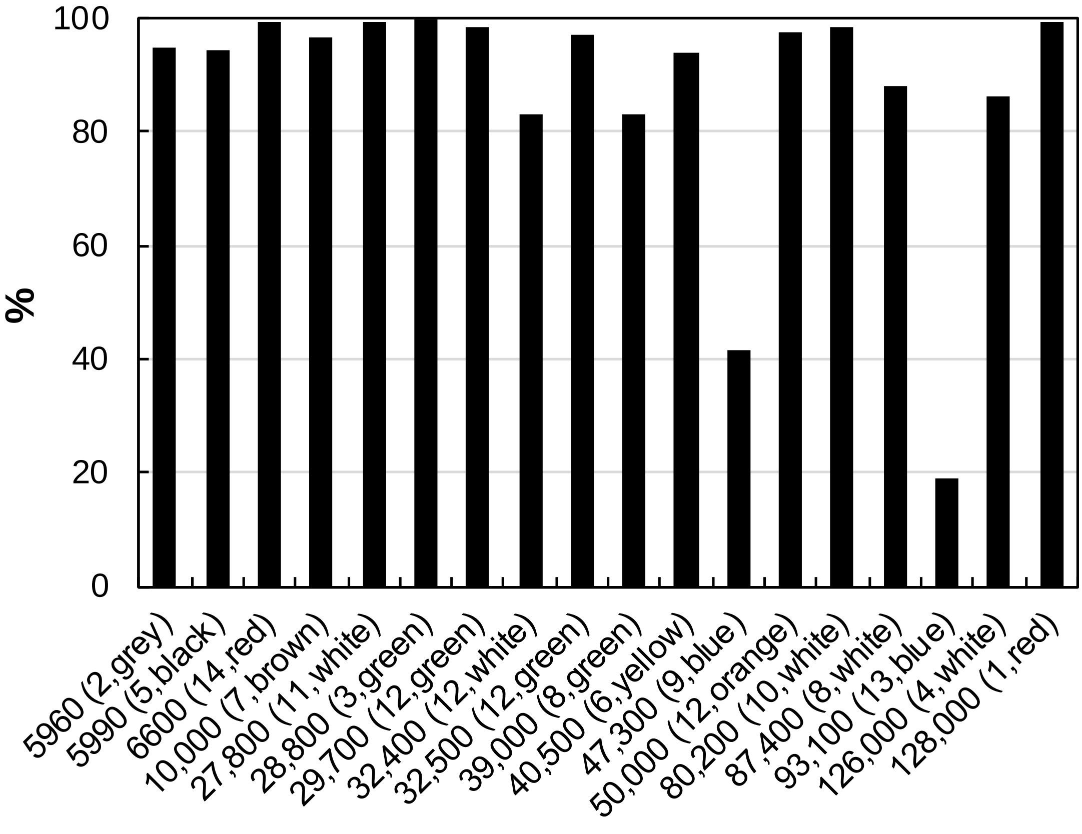
The 20 mm lip area of samples that had been subject to acetic acid extraction for 24 h usually exhibited a distinct fading and a reduction in sheen of the enamelled surface that was most marked on the brighter colours and least noticeable on any gold leaf décor. In a few cases, discolouration extended beyond the lip line suggesting that acidic vapour was also able to react with some applications, while in one case, the entire enamel within the lip area had completely corroded, resulting in an accumulation of coloured particulates at the bottom of the extract. Samples subject to extraction in Coca Cola exhibited limited but noticeable fading of colour of the enamelled areas, with a reduction in sheen and brown staining also evident on some of the paler colours. Significantly, a number of areas having undergone extraction shed small quantities of material as a powder when subsequently dried and wiped with two-ply blue roll.

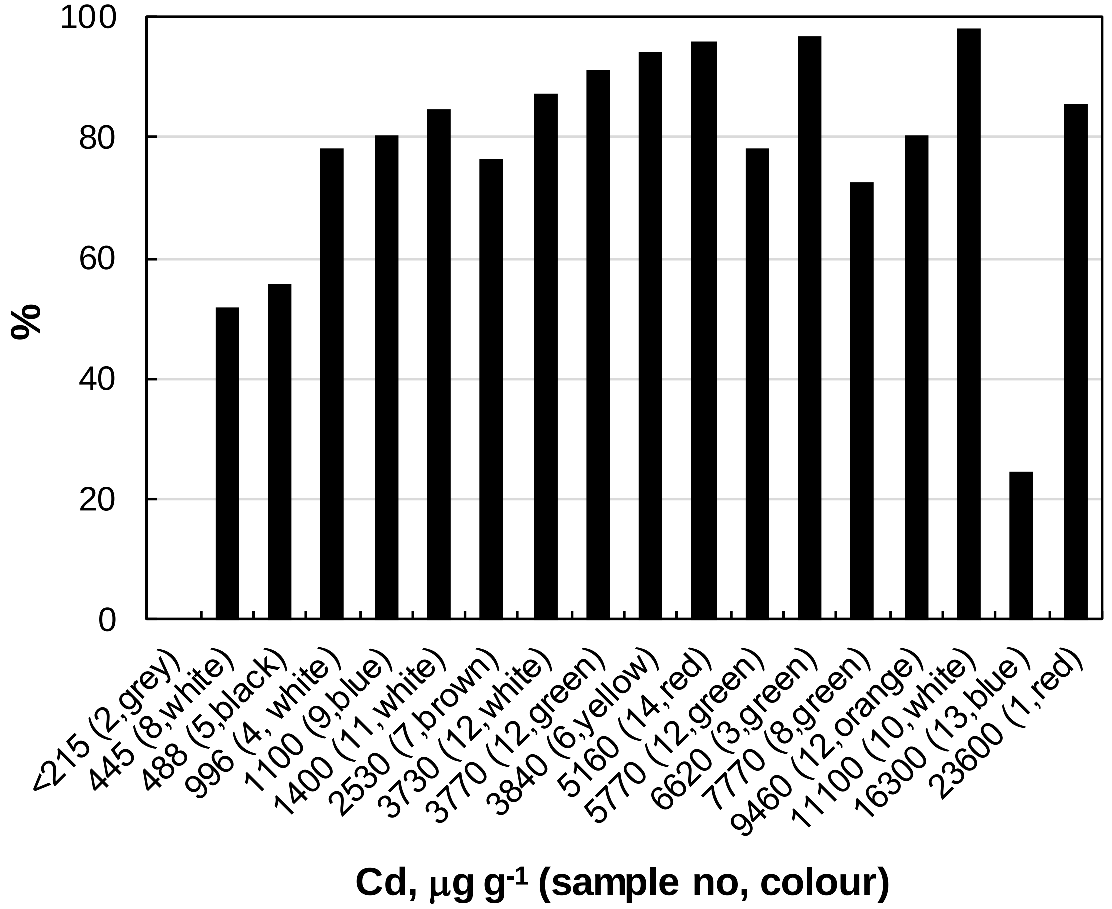
Table 2: Quantities and volume-normalised concentrations of Pb and Cd extracted by acetic acid and Coca Cola from drinking glassware decorated within the lip area and as determined by ICP (Pb^{ext} and Cd^{ext}, respectively). Also shown are the estimated percentage of the lip area that is decorated, 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
4% acetic acid									
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	
Coca Cola Classic									
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	

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

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





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

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

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

4. Discussion

4.1. Nature of Pb and Cd in the enamelled glassware

The widespread occurrence of Pb in the enamelling of glassware used to consume beverages is consistent with the pervasive application of PbO in the flux to lower the melting point of the glass-forming components (Beldì et al., 2016). That adjacent areas of different colour on the same item often contained Pb concentrations that differed by about an order of magnitude, however, suggests leaded pigments are also employed in the enamelling process. These include the brightly coloured lead antimonide (yellow) and lead chromates (yellow-orange-red), and green chromic oxide, produced by the thermal decomposition of $PbCrO_4$ (Lehman, 2002).

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

4.2. Regulatory compliance of enamelled glassware

Legislation in Europe relating to Pb in paint can be traced back more than a century, with concentration limits in consumer formulations being progressively revised downwards (Bodel, 2010). Because high quality and cost-effective alternative pigments and driers are now available, the current maximum concentration for Pb in consumer paints and enamels is 90 μg g^{-1} in the dry film in many countries (Gottesfeld et al., 2014). With regard to lead chromates, the EU has recently constrained their availability to certain professions and industries and restricted the supply to one particular company based in Canada (REACH, 2016). While there has been less documentation of the content and effects of Cd in paints, the metal is currently restricted by Annex XVII of REACH to a concentration of 100 μg g^{-1} in consumer paints with the exception of formulations containing more than 10% Zn, and to 1000 μg g^{-1} on painted articles (Commission Regulation, 2016).

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

Non-compliant samples include both old and new products that encompass all categories of drinking glassware with the exception of jars.

Extractable concentration limits for the lip area and based on immersion in 4% acetic acid are also stipulated by Proposition 65 as 0.5 and 4 mg L^{-1} for Pb and Cd respectively (Calderwood and Bopp, 2005). With reference to Table 2, all but one item tested (excluding the control) would be non-compliant and require a warning label based on acid-extractable Pb, while five items, including two purchased new, would require a warning based on extractable Cd. Despite concentrations of Pb extracted by Coca Cola being significantly lower than those mobilised by acetic acid (presumably because lead phosphate is considerably less soluble than lead acetate), the Proposition 65 limit was exceeded in all cases for this extractant with the exception of the control; in contrast, although release of Cd was less dependent on the extraction medium, concentrations mobilised by Coca Cola were always below the Proposition 65 limit.

While some countries have recently adopted similar, volume-normalised concentration limits for the acid-extraction of Pb and Cd from the lip area of decorated drinking glasses (e.g. Health Canada, 2016), others have defined safety requirements on mass limits on metal migration. For instance, in Poland, and according to PN-B 13210:1997, the total quantity of Pb or Cd extracted by 4% acetic acid per product must not exceed 2 mg and 0.2 mg, respectively (Rebaniak et al., 2014). On this basis, and according to Table 2, all but three items tested accordingly in the present study (excluding the control) would be non-compliant for Pb (with many samples releasing more than 10 mg), and all but five items would be non-compliant for Cd (with a maximum migration of over 5 mg).

4.3. The wider problem

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

The presence of hazardous elements in decorated glassware has implications for both human exposure and the environment. Regarding the former, direct ingestion may occur through the consumption of beverages in drinkware that is decorated within the lip area, with exposure accentuated for hot or acidic drinks and for enamel that is deteriorating; of particular concern in this respect is densely decorated glassware that is specifically designed for use by children (e.g. see Figure 3). Indirect ingestion may also occur via the handling of enamelled surfaces or through contamination of other food-contact items should surfaces be abraded during washing or stack-storage. Persistent use of a dishwasher is also known to cause decorative enamels to ‘fade’, but a warning to this effect was stated on the packaging of only about one half of the drink-ware products purchased new. With respect to the environment, the recycling of decorated container glass like bottles and jars acts to introduce hazardous elements into the post-consumer cullet, while landfilling of decorated drinking glassware that cannot be recycled affords a means by which these elements enter groundwater through leaching.

5. Conclusions

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

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References

Ajmal, M., Khan, A., Nomani, A.A., Ahmed, S., 1997. Heavy metals: leaching from glazed surfaces of tea mugs. Science of the Total Environment 207, 49-54.

ASTM, 2009. Standard test method for lead and cadmium extracted from the lip and rim area of glass tumblers externally decorated with ceramic glass enamels. C927 – 80, West Conshohocken, PA.

Beldì, G., Jakubowska, N., Peltzer, M.A., Simoneau, C., 2016. Testing approaches for the release of metals from ceramic articles: In support of the revision of the Ceramic Directive 84/500/EEC. Publications Office of the European Union, Luxembourg, 86pp.

Bodel, R., 2010. Lead Legislation: The World’s best and worst practice regulating lead in paint. The LEAD Group Incorporated, Summer Hill, Australia, 10 pp.

Calderwood, J.A., Bopp, A., 2005. Summary of California Proposition 65 Settlement Related to Lead and Cadmium Exposure from Outside Surfaces of Glass and Ceramicware. Society of Glass and Ceramic Decorators, Alexandria, VA, 7pp.

Commission Regulation, 2016. Amendment of Annex XVII to Regulation (EC) No 1907/2006 of the European Parliament and of the Council concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards cadmium. Official Journal of the European Union L 40/5.

Council of the European Communities, 1984. Council Directive 84/500/EEC of 15 October 1984 on the approximation of the laws of the Member States relating to ceramic articles intended to come into contact with foodstuffs. Official Journal of the European Communities No. L 277/12.

Demont, M., Boutakhrit, K., Fekete, V., Bolle, J., Van Loco, J., 2012. Migration of 18 trace elements from ceramic food contact material: Influence of pigment, pH, nature of acid and temperature. Food and Chemical Toxicology 50, 734-743.

Dong, Z.H., Lu, L.X., Liu, Z.G., 2015. Migration model of toxic metals from ceramic food contact materials into acid food. Packaging Technology and Science 28, 545-556.

Gottesfeld, P., Pokhrel, D., Pokhrel, A.K., 2014. Lead in new paints in Nepal. Environmental Research 132, 70-75.

Hamer, F., and Hamer, J. 2004. The Potter’s Dictionary of Materials and Techniques. A & C Black, London, 439pp.

Health Canada, 2016. Consumer product safety: Glazed ceramics and glassware regulations - Dealer information. http://www.hc-sc.gc.ca/cps-spc/pubs/indust/ceramics-ceramiques/index-eng.php (accessed June 2017).

Henden, E., Cataloglu, R., Aksuner, N., 2011. Determination of arsenic leaching from glazed and non-glazed Turkish traditional earthenware. Science of the Total Environment 15, 2993-2996.

Kiddell, P., 2015. Understanding ceramic and glass decorating – Inks. Federation of European Screen Printers Associations https://www.fespa.com/news/features/understanding-ceramic-and-glass-decorating-part-one.html (Accessed June 2017)

Lehman, R., 2002. Lead Glazes for Ceramic Foodware. The International Lead Management Center, Research Triangle Park, NC, 193pp.

Mead, M.N., 2010. Cadmium confusion: Do consumers need protection? Environmental Health Perspectives 118, A528-A534.

Office of Environmental Health Hazard Assessment, 2016. Proposition 65: The Safe Drinking Water and Toxic Enforcement Act of 1986. California Environmental Protection Agency https://oehha.ca.gov/proposition-65 (accessed June 2017)

REACH, 2016. Newsletter, Dec. 2016, SGS, Ellesmere Port, UK http://www.sgs.co.uk/~/media/Local/UK/Documents/Brochures/SGS%20CRS%20REACH%20Newsletter%20Issue%207%20LR%2016%2012.pdf accessed June 2017.

Rebeniak, M., Wojciechowska-Mazurek, M., Mania, M., Szynal, T., Strzelecka, A., Starska, K., 2014. Exposure to lead and cadmium released from ceramics and glassware intended to come into contact with food. Roczniki Państwowego Zakładu Higieny 65, 301-309.

Sheets, R.W., 1999. Acid extraction of lead and cadmium from newly-purchased ceramic and melamine dinnerware. Science of the Total Environment 234, 233-237.

Weidenhamer, J.D., Fitzpatrick, M.P., Biro, A.M., Kobunski, P.A., Hudosn, M.R., Corbin, R.W., Gottesfeld, P., 2017. Metal exposures from aluminum cookware: An unrecognized public health risk in developing countries. Science of the Total Environment 579, 805-813.

Zhao, H., Xia, B., Fan, C., Zhao, P., Shen, S., 2012. Human health risk from soil heavy metal contamination under different land uses near Dabaoshan Mine, Southern China. Science of the Total Environment 417-418, 45-54.

Ziegler, S., Wolf, C., Salzer-Muhar, U., Schaffer, A., Konnaris, C., Ruediger, H., Osterode, W., 2002. Acute lead intoxication from a mug with a ceramic inner surface. The American Journal of Medicine 112, 677-678.

Zuckerman, M.A., Savory, D., Rayman, G., 1989. Lead encephalopathy from an imported Toby mug. Postgraduate Medical Journal 65, 307-309.