Leaded electronic waste is a possible source material for lead-contaminated jewelry

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Abstract

Highly leaded jewelry, often imported from China, remains widely available in the United States. Leaded electronic waste is exported from the United States to several Asian countries where solder is recovered and circuit boards are stripped of parts in small workshops. To assess whether electronic waste is being recycled into the jewelry, lead, tin and copper content of highly leaded jewelry samples were determined by atomic absorption spectrometry. Sixteen jewelry items previously determined to contain 20–80% lead by weight were analyzed. Samples were digested in nitric acid for analysis of lead and copper, and in aqua regia for analysis of tin. Six samples contained significant amounts of tin, from 20.8% to 29.9% by weight. In addition, copper was a significant minor component of five of these samples (up to 4% by weight). Copper (present at 10–40% by weight in circuit boards) was shown to rapidly move into heated lead–tin solder. The combined lead–tin–copper content of these six items ranges from 93.5% to 100%, suggestive of a solder-based source material. These results are consistent with the hypothesis that recycled circuit board solders are being used to produce some of the heavily leaded imported jewelry sold in the United States. Should this hypothesis be substantiated, it suggests that environmental policies to protect children’s health must address both proper recycling of source materials as well as restrictions of the lead content in consumer goods.

Keywords: Lead; Jewelry; Neurotoxicity; Children’s health; Electronic waste

1. Introduction

Electronic waste (e-waste) disposal is a growing problem (Kang and Schoenung, 2005). It is estimated that 100 million obsolete computers, monitors and televisions are disposed of annually in the US (Hileman, 2006). Quantities of e-waste are increasing due both to greater reliance on electronic devices and decreasing lifespan of computers and other electronics (Kang and Schoenung, 2005). E-waste contains a number of potentially harmful substances, including metals such as lead (in lead–tin solders, and leaded glass of cathode ray tubes or CRTs), cadmium (in switches and solder joints), and antimony (used as a flame retardant in the form of its trioxide), and organic compounds such as polybrominated diphenyl ethers (PBDEs) (Ernst et al., 2003; Brigden et al., 2005).

To address problems created by e-waste, new regulations and laws have been implemented in Europe and the United States. The European Directive on Waste Electrical and Electronic Equipment (WEEE) became effective in August 2005 and requires manufacturers to assume responsibility for collection, recovery and responsible disposal of e-waste (European Union, Directives 2003a, 2003b; Liu, 2006). The Chinese government has also adopted legislation to control pollution from e-waste (Kang and Schoenung, 2005). The US initiatives include bans on disposal of CRTs in several states, and California’s Electronic Waste Recycling Act (2003) requires manufacturers of electronics to either collect obsolete devices or pay an alternative fee for recycling of e-waste (Kang and Schoenung, 2005).

Environmental organizations (Basel Action Network, 2002; Brigden et al., 2005) have drawn attention to the...
large amount of e-waste that is being shipped from developed nations, particularly the US, to countries in east Asia such as China where environmental regulations are less strict and/or enforcement much weaker. While some recycling of this e-waste takes place, numerous instances of severe environmental contamination and hazards to workers have been documented (Basel Action Network, 2002; Brigden et al., 2005). The processing procedures observed in small Chinese workshops include the heating of printed circuit boards on coal stoves in puddles of solder to loosen the other electronic components for recovery (Fig. 1). The remaining solder on the boards is knocked off into collection buckets (Puckett, Personal communication). The fate of materials such as the solder collected in these recycling operations has not been reported and is unknown.

Reebok International Ltd. recently recalled 300,000 charm bracelets after a four-year-old child who swallowed a heart-shaped charm that was found to contain over 99% lead by weight died of lead poisoning (Associated Press, 2006; CDC, 2006). These bracelets were imported from China. Despite US Consumer Product Safety Commission (CPSC) guidelines requiring a maximum lead content of 0.06% by weight in children’s and costume jewelry (US CPSC, 2005), and frequent recalls of leaded items (US CPSC, 2004, 2006a,b,c), lead contamination of jewelry remains widespread. While lead-based paint is still regarded as the major source of lead exposure for young children in the United States, exposures to lead from other sources can still be significant. Recent studies indicating that concentrations of lead substantially lower than the current Centers for Disease Control and Prevention’s threshold level of concern (10 µg per deciliter) result in significant intellectual impairment in children (Needleman and Gatsonis, 1990; Lanphear et al., 2000; Canfield et al., 2003) have brought renewed attention to other potential sources of lead exposure for children, such as leaded jewelry.

In a 2005 study, an average content of 30.6% lead by weight was found in 285 pieces of jewelry purchased at 20 different stores (Maas et al., 2005). Wipe tests showed significant amounts of accessible lead in many of the pieces containing more than 3.0% lead. Recent tests in our laboratory confirm these results. Of 139 jewelry samples purchased at 10 different retail chains, almost half were heavily leaded (>80% lead by weight), and the average lead content was 44.0%. Almost all of the highly leaded items were imported from China (Weidenhamer and Clement, 2007). The specific objective of this study was to determine whether recycled solder is a possible source material for the lead in some highly leaded costume jewelry based on elemental analysis of lead, tin, and copper in the jewelry products.

2. Materials and methods

2.1. Samples

Jewelry samples used in this study were selected from a collection of 139 samples purchased in May 2006 at retail stores in the US Analysis of these samples for lead has previously been reported (Weidenhamer and Clement, 2007). For the purpose of this investigation, a subset of jewelry items with components containing 20–80% lead by weight was selected for analysis of lead, tin, and copper content (sixteen samples total). Thirteen of these items were labeled as imported from China, while the origin of three items was uncertain from product labels. Jewelry items with very high lead content (>80% by weight) were excluded from this
study given that the typical content of electronic solders is 60% tin/40% lead or 63% tin/37% lead by weight (Geibig and Socolof, 2005). The study also included recovered solder samples collected from the floor of a workshop in Taizhou, China by Greenpeace volunteers in coordination with the Basel Action Network (Seattle, WA). Because of the heterogeneity of this material, eight replicate samples were analyzed.

2.2. Sample preparation

All samples were stored in plastic bags to prevent cross-contamination. All glassware was rinsed with conc. nitric acid prior to use. Handheld pliers were used to clip small sections (0.1–0.2 g) from each item. The pliers were cleaned in between samples to prevent carryover. Each sample was analyzed in duplicate using two digestion procedures. All replicate samples were taken from the same jewelry component (charm, pendant, etc.). (a) Digestion in conc. nitric acid (Maas et al., 2005; Weidenhamer and Clement, 2007) was used for the determination of lead and copper.

2 min of heating. Thus the presence of significant amounts of copper in most of these samples is consistent with an origin from recovered solder. This is confirmed by the analysis of solder samples recovered from a workshop in Taizhou, China, which contained an average of 4.35% copper (Table 2). Analyses of four other solder samples recovered from Asian workshops have recently been reported by Brigden et al. (2005), and these data, which show copper contents of 0.21–0.90%, are summarized in Table 2.

The overall proportion of lead to tin in these samples deviates from that expected for typical electronic solders. While analysis of recovered solders (Table 2) found 46.3–55.0% tin and 35.8–38.5% lead by weight, reasonably close to the expected 60% tin/40% lead ratio of most electronic solder, the jewelry samples had a much higher proportion of lead (mean 70.1%, Table 1) in comparison to tin (mean 24.6%). This could indicate either that these samples are
225 not derived from solder, or alternately that recycled electronic solder is being mixed with other scrap lead materials such as battery lead in the production of this inexpensive jewelry. Indeed, it seems unlikely that the metals for these jewelry items are specifically formulated to a certain composition. Multiple analyses of charms from the recalled Reebok bracelets showed highly variable lead content.

232 Individual samples tested by Minnesota laboratories were found to contain 99.1%, 67.0% and 0.07% lead by weight (CDC, 2006). Such variability of lead content suggests opportunistic use of source materials for this jewelry, one of which may be recovered solders. The fact that such a high proportion of the mass of these samples is accounted for by lead, tin and copper suggests that this possibility is worth closer scrutiny.

239 It should be clarified that this study excluded a significant number of very heavily leaded samples from our original dataset (Weidenhamer and Clement, 2007) which contained more than 80% lead by weight, as these samples were considered unlikely to originate from electronic solders with original concentrations of approximately 40% lead by weight. Work to identify potential source materials of these very heavily leaded items has also been undertaken and will be reported separately (Weidenhamer and Clement, unpublished results). Thus, our conclusion is that recovered electronic solders are a potential source material for some but by no means all highly leaded jewelry.

246 The global trade in lead includes not only leaded products imported from China such as the jewelry examined in this study, but also large quantities of e-waste that are exported from the United States to a number of poorer nations, including China. This waste represents a large potential source of lead for use in other materials. The data presented in the paper support a novel hypothesis of the

Table 1

<table>
<thead>
<tr>
<th>Jewelry Item (identification code)</th>
<th>Component analyzed</th>
<th>Country of origin</th>
<th>% Pb</th>
<th>% Sn</th>
<th>% Cu</th>
<th>Total Pb + Sn + Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stretch bracelet (A20)</td>
<td>Bracelet link</td>
<td>China</td>
<td>60.2</td>
<td>30.7</td>
<td>5.0</td>
<td>95.9</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>64.8</td>
<td>29.9</td>
<td>3.7</td>
<td>98.4</td>
</tr>
<tr>
<td>Charm bracelet (A26)</td>
<td>Charm</td>
<td>China</td>
<td>67.1</td>
<td>23.7</td>
<td>0.05</td>
<td>90.8</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>73.0</td>
<td>23.4</td>
<td>0.05</td>
<td>96.4</td>
</tr>
<tr>
<td>Charm bracelet (M12)</td>
<td>Charm</td>
<td>Unknown</td>
<td>67.7</td>
<td>24.3</td>
<td>1.1</td>
<td>93.1</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>66.6</td>
<td>24.6</td>
<td>0.9</td>
<td>92.1</td>
</tr>
<tr>
<td>Charm bracelet (M15)</td>
<td>Charm</td>
<td>China</td>
<td>73.6</td>
<td>20.8</td>
<td>1.2</td>
<td>95.6</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>78.2</td>
<td>20.8</td>
<td>1.7</td>
<td>90.7</td>
</tr>
<tr>
<td>Key chain with locket (M43)</td>
<td>Locket</td>
<td>China</td>
<td>71.7</td>
<td>23.1</td>
<td>3.8</td>
<td>98.6</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>65.7</td>
<td>24.7</td>
<td>4.1</td>
<td>94.9</td>
</tr>
<tr>
<td>Charm bracelet (M54)</td>
<td>Charm</td>
<td>China</td>
<td>71.9</td>
<td>24.0</td>
<td>5.2</td>
<td>96.6</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>70.9</td>
<td>26.8</td>
<td>1.1</td>
<td>98.6</td>
</tr>
<tr>
<td>Mean of above samples</td>
<td></td>
<td></td>
<td>71.4</td>
<td>25.4</td>
<td>3.2</td>
<td>100.0</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>70.1</td>
<td>24.6</td>
<td>2.24</td>
<td>96.9</td>
</tr>
</tbody>
</table>

Values of each replicate analysis are shown with averages.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Source</th>
<th>% Pb</th>
<th>% Sn</th>
<th>% Cu</th>
<th>Total Pb + Sn + Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solder workshop sample (n = 8)</td>
<td>Taizhou, China</td>
<td>35.8</td>
<td>55.0</td>
<td>4.35</td>
<td>95.2</td>
</tr>
<tr>
<td>CH05011&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Guiyu, China</td>
<td>37.5</td>
<td>48.5</td>
<td>0.90</td>
<td>86.9</td>
</tr>
<tr>
<td>CH05026&lt;sup&gt;b&lt;/sup&gt;</td>
<td>Guiyu, China</td>
<td>38.5</td>
<td>49.8</td>
<td>0.73</td>
<td>89.0</td>
</tr>
<tr>
<td>IT04002&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Zarfarabad, India</td>
<td>36.2</td>
<td>46.3</td>
<td>0.21</td>
<td>82.7</td>
</tr>
<tr>
<td>IT05009&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Shashtri Park, India</td>
<td>37.5</td>
<td>49.8</td>
<td>0.27</td>
<td>87.6</td>
</tr>
</tbody>
</table>

<sup>a</sup> From heated metal plate in small workshop.
<sup>b</sup> From floor of solder separation and recovery workshop.
<sup>c</sup> From solder recovery workshops; analyses reported in Brigden et al. (2005).
reycling of e-waste into consumer products. The evidence presented here suggests that at least some highly leaded jewelry may be manufactured from scrap solder materials, possibly mixed with other scrap sources of lead such as battery lead. Should this hypothesis be borne out, it would suggest that environmental policies need to address both the proper recycling of e-waste as well as restrictions on lead in consumer goods such as jewelry.

4. Uncited reference


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References


Puckett, J., Personal communication.


