Characterization and Analysis of Airborne Metal Exposures Among Electronic Scrap Valuation Workers- Shredding

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Abstract—
Recycling is the most appropriate final step in the electronics life cycle. Certain materials contained in electronics can be environmental and occupational health concerns. More information is needed to properly assess occupational health risks presented by recycling operations. A quantitative airborne metal exposure survey was conducted on workers shredding printed circuit boards. Aluminum, arsenic, beryllium, calcium, cadmium, chromium, copper, iron, lead, magnesium, manganese, nickel, selenium, sodium and zinc were all well below permissible exposure levels (PEL). Airborne silver exposures were above the PEL 11.0 percent of the time. Attempts to correlate air sample results with concurrently collected bulk sample metal concentrations were not successful. The Untha shear shredder equipped with ventilation, as is typical in the industry, represents a minimal inhalation hazard regarding silver and no inhalation hazard to the operators for all other metals studied.

Keywords- electronic scrap; airborne metal exposure; shredding; ventilation

I. INTRODUCTION
Electronics derived scrap (E- scrap) is one of the fastest growing scrap streams today and subject of emerging European Union directives and state regulation regarding end-of-life management of electrical and electronic products. Two outlets exist for electronic scrap; placement into landfills and recycling. Recycling is preferred as valuable metals are reclaimed and precious landfill space conserved. Intact, electronic equipment is not hazardous; however, the individual components may contain a number of potentially hazardous materials, such as lead and cadmium. Electronics recycling is of interest to the occupational health profession due to the presence of hazardous materials in the electronic scrap stream and the potential for worker exposure during reclamation processes. This study characterizes operator airborne metal exposures, work practices, and engineering controls used during shredding of printed circuit boards. There are four principle steps in the electronic scrap valuation process: shredding, roasting, milling, and melting. The purpose of this industrial hygiene survey was to characterize processes, work practices, engineering controls and airborne concentrations of metals generated during typical electronic scrap valuation, and recycling operations. Information was collected to help answer the following questions about the first step in the process; shredding:

1. What are the airborne metal exposure levels of workers performing typical printed circuit board shredding?
2. How do these exposure levels compare to the respective Occupational Safety and Health Administration (OSHA) PELs and other Occupational Exposure Limits (OEL)?
3. What concentration of metals existed in the printed circuit boards on the days air sampling was conducted?
4. What is the nature of engineering controls used to control dust?
5. What tasks do the operators perform that could contribute to exposure?
6. Is there a correlation between air and bulk sample results?

II. PROCESS AND EQUIPMENT DESCRIPTION
This study characterizes exposures occurring during operation of an Untha shear shredder with a capacity of 2500 lbs per hour. The shredding process has 7 components: unloading of Gaylord boxes, vibratory table, transfer conveyor between the vibratory table and the shredder, the shredding unit, a second vibratory table, transfer conveyor between the table and product sampler and the final product sampler.

The shredding mill operator receives cardboard Gaylord boxes containing circuit boards. Scrap containers are loaded onto a tilt lift station and the material is pulled from the container onto a shaker table that transfers the product to the conveyor. The Untha shear shredder reduces scrap size to less than one inch. All input material is shredded and conveyed to the vibratory table and the shredder, the shredding unit, a second vibratory table, transfer conveyor between the table and product sampler. The ten percent sample of the shredded material is collected in a 55-gallon drum and then sent into the precious metal assay processes. The remaining ninety percent of the material is collected and stored in bulk sacks. Two workers perform the following tasks during the shift: material
handling, loading shredder, shredder operator inspection, product sampler inspection, changing the sampling containers, changing the bag house drop out drum, housekeeping and administrative duties.

III. METHODS

A. Air Samples

Twenty-eight 8-hour personal air samples were collected over a 3-week sampling period assessing the total mass of 16 metals present in the breathing zones of workers shredding printed circuit boards at United Recycling, Franklin Park, IL. Methods specified in the OSHA Technical Manual and the National Institute for Occupational Safety and Health (NIOSH) Manual of Analytical Methods [1] were used for sample collection and analysis. Sample analysis was performed at an AIHA accredited laboratory for aluminum, arsenic, beryllium, calcium, cadmium, chromium, copper, iron, lead, magnesium, manganese, nickel, selenium, silver, sodium, and zinc.

A qualitative exposure assessment was used to judge which tasks performed within a given job are most likely resulting in the highest exposure. This information is used to prioritize future task sampling efforts and determine Short Term Exposure Limit (STEL) exposures.

The type and design specifications of engineering control equipment used and hood locations were recorded. Ventilation flow rates were measured using a Shortridge Air Data Meter.

Exposure data was analyzed in accordance with typical statistical principles [2]. For airborne metal exposure data, we calculated descriptive statistics, central tendency, and characteristics of the upper tail of the distribution. For the latter, we calculated the 95% upper confidence limit (UCL) for the 95\textsuperscript{th} percentile of the distribution (the upper tolerance limit (UTL) [3] and for the fraction of the distribution that exceeded the PEL and listed OEL’s [4]. Exceedance fractions provide information on the proportion of the distribution that exceeds a given exposure value. The uncertainty around point estimates is described by the 95 % UCL. A set of exposure measurements is generally considered to be well controlled if the exceedance fraction is less than or equal to 5 % and the geometric standard deviation (GSD) below 2.5 [5]. Values below the detection limit were divided by two for all statistical analyses.

Exposure data for this study were compared to current OSHA PEL values for each respective metal [6]. Results are also compared to other OEL’s such as the Department of Energy (DOE) [7]. OSHA PEL values are as follows: Aluminum (15 mg/m\textsuperscript{3}), Arsenic (0.01 mg/m\textsuperscript{3}), Beryllium (0.002 mg/m\textsuperscript{3}), Calcium (15 mg/m\textsuperscript{3}), Cadmium (0.005 mg/m\textsuperscript{3}), Chromium (1.0 mg/m\textsuperscript{3}), Copper (1.0 mg/m\textsuperscript{3}), Iron (10 mg/m\textsuperscript{3}), Lead (0.05 mg/m\textsuperscript{3}), Magnesium (15 mg/m\textsuperscript{3}), Manganese (5 mg/m\textsuperscript{3}), Nickel (1.0 mg/m\textsuperscript{3}), Selenium (0.2 mg/m\textsuperscript{3}), Silver (0.01 mg/m\textsuperscript{3}), Sodium (NA), Zinc (5 mg/m\textsuperscript{3}).

B. Bulk Samples

Representative bulk samples were collected concurrently with air samples to allow inter-lot metal concentration comparisons and to examine if relationships exist between air sampling results and processed metal concentrations. Approximately 0.75- 1.0 Kg, out of a lot size averaging 1500 kilograms, of whole circuit boards were randomly selected over the course of the shift by the shredding operators via periodic grab samples. Each bulk sample contained approximately 5-6 circuit boards, which were then subsequently roasted at 900 degrees F to remove combustible materials leaving metallics behind. Sample weights after roasting ranged between 0.3-0.4 Kg. These samples were then double bagged in Ziploc \textsuperscript{®} bags and packaged for shipment to the laboratory for analysis.

To achieve homogeneity, the bulk samples were ball milled and sieved to 20 mesh, mimicking the milling parameters used at URI. A 1.0-gram sample was then analyzed according to NIOSH method 7300.

IV. Results

A. Airborne Metal Exposure Characterization (Table 1)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Mean (mg/m\textsuperscript{3})</th>
<th>GSD</th>
<th>95\textsuperscript{th}/95UTL (mg/m\textsuperscript{3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>0.012</td>
<td>1.61</td>
<td>0.029</td>
</tr>
<tr>
<td>Lead</td>
<td>0.005</td>
<td>1.5</td>
<td>0.012</td>
</tr>
<tr>
<td>Silver</td>
<td>0.005</td>
<td>1.5</td>
<td>0.012</td>
</tr>
</tbody>
</table>

- All exposure measurements for these metals were below respective OSHA PEL’s and expected to be below the OSHA PEL greater than 99 percent of the time. In addition, all airborne beryllium exposures were below the Department of Energy’s action limit of 0.0002 mg/m\textsuperscript{3} and statistical analysis demonstrated that exposures are anticipated to be below this limit greater than 99 percent of the time.

Lead:
- The mean of the lead samples was 0.012 mg/m\textsuperscript{3}, with a geometric mean (GM) of 0.011 mg/m\textsuperscript{3}, a GSD of 1.61 and a 95\textsuperscript{th}/95UTL of 0.029 mg/m\textsuperscript{3}. Exposures are anticipated to be below the OSHA PEL of 0.05 mg/m\textsuperscript{3} greater than 99 percent of the time. There is high confidence (> 95%) that less than five percent of samples may exceed the OSHA action level of 0.030 mg/m\textsuperscript{3}.

Silver:
- The mean of the silver samples was 0.005 mg/m\textsuperscript{3}, with a GM of 0.005 mg/m\textsuperscript{3}, a geometric standard deviation of 1.5 and a 95\textsuperscript{th}/95UTL of 0.012 mg/m\textsuperscript{3}. Therefore, we lack confidence that less than five percent of samples might exceed the OSHA PEL of 0.01 mg/m\textsuperscript{3}.
### TABLE 1
DESCRIPTIVE STATISTICS OF AIRBORNE METAL EXPOSURE DATA (mg/m³)

<table>
<thead>
<tr>
<th>Metal:</th>
<th>N</th>
<th>Mean (SD)</th>
<th>Geometric Mean (GSD)</th>
<th>Range</th>
<th>95th percentile UTL</th>
<th>PEL exceedance UCL (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>28</td>
<td>0.017 (0.012)</td>
<td>0.014 (1.8)</td>
<td>(0.004–0.06)</td>
<td>0.055</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Arsenic</td>
<td>28</td>
<td>All values &lt; LOD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Beryllium</td>
<td>28</td>
<td>0.000013 (0.000006)</td>
<td>0.000001 (1.5)</td>
<td>(0.000007–0.00004)</td>
<td>0.000028</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Calcium</td>
<td>28</td>
<td>0.045 (0.023)</td>
<td>0.040 (1.6)</td>
<td>(0.018–0.11)</td>
<td>0.12</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Cadmium</td>
<td>28</td>
<td>0.001 (0.001)</td>
<td>0.0004 (2.1)</td>
<td>(0.0002–0.0031)</td>
<td>0.002</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Chromium</td>
<td>28</td>
<td>0.0005 (0.0001)</td>
<td>0.0004 (1.3)</td>
<td>(&lt;0.0004–0.0011)</td>
<td>0.0007</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Copper</td>
<td>28</td>
<td>0.032 (0.015)</td>
<td>0.030 (1.5)</td>
<td>(0.015–0.091)</td>
<td>0.073</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Iron</td>
<td>28</td>
<td>0.020 (0.010)</td>
<td>0.019 (1.5)</td>
<td>(0.009–0.062)</td>
<td>0.045</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Lead</td>
<td>28</td>
<td>0.012 (0.009)</td>
<td>0.011 (1.6)</td>
<td>(0.006–0.052)</td>
<td>0.029</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Magnesium</td>
<td>28</td>
<td>0.005 (0.002)</td>
<td>0.004 (1.4)</td>
<td>(0.002–0.008)</td>
<td>0.009</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Manganese</td>
<td>28</td>
<td>0.001 (0.001)</td>
<td>0.001 (1.9)</td>
<td>(0.0003–0.0051)</td>
<td>0.003</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Nickel</td>
<td>28</td>
<td>0.005 (0.004)</td>
<td>0.004 (1.6)</td>
<td>(0.002–0.020)</td>
<td>0.013</td>
<td>&lt;1.0</td>
</tr>
<tr>
<td>Selenium</td>
<td>28</td>
<td>All values &lt; LOD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td>25</td>
<td>0.005 (0.002)</td>
<td>0.005 (1.5)</td>
<td>(0.0019–0.0083)</td>
<td>0.012</td>
<td>11.2</td>
</tr>
<tr>
<td>Sodium</td>
<td>28</td>
<td>0.012 (0.003)</td>
<td>0.012 (1.3)</td>
<td>(0.005–0.018)</td>
<td>0.020</td>
<td>NA</td>
</tr>
<tr>
<td>Zinc</td>
<td>28</td>
<td>0.009 (0.011)</td>
<td>0.007 (2.0)</td>
<td>(0.003–0.059)</td>
<td>0.034</td>
<td>&lt;1.0</td>
</tr>
</tbody>
</table>

*95th percentile upper tolerance limit (UTL) – upper 95% confidence limit about the 95th percentile of the distribution. b Occupational exposure limit exceedance fraction upper confidence limit (UCL) – upper 95% confidence limit for fraction of samples that exceed a given occupational exposure limit.

B. Bulk Sample Analysis
The average concentration (ppm) of the following metals present in the roasted samples (N=19) were: Aluminum (20,000), Arsenic (34), Beryllium (10), Calcium (46,000), Cadmium (27), Chromium (132), Copper (254,000), Iron (21,000), Lead (5000), Magnesium (1800), Manganese (1000), Nickel (4500), Selenium (<60), Silver (90), Sodium (1450) and zinc (4100).

C. Engineering Control Analysis
Exhaust hoods were typical partial enclosures for the shredder and the product sampler. Hoods used for elevation charges between conveyance systems were canopy style. A 2000 CFM dust collector equipped with typical course aerosol collection bags ventilates the shredding unit (725 CFM), vibrator table hood (210 CFM), hood for material drop off from vibratory conveyor onto sampling conveyor (210 CFM) and the hood for product sample collection (850 CFM).

D. Qualitative Exposure Assessment
Visual observation of typical operator tasks revealed that metal exposures were most likely created by changing sampler containers, changing the dust collector drum, product sampler inspection, and housekeeping.
E. Relationships Between Operator Airborne Metal and Mean Concentrations of Metals in Concurrently Collected Bulk Samples

Adjusted R-square values (not significant) were calculated to assess the degree in which airborne metal concentrations experienced by the shredding operators were a function of the concentration of the metal in the circuit boards. It is postulated that as material flows through the four processing steps the correlation between the bulk samples and the air samples could increase. An increase in the correlation is possible as the material processed becomes smaller and more easily entrained into the air. If correlations exist between copper or precious metals content of the base material, which are determined for each lot, and airborne exposure, it may be possible to determine relative operator exposures to occupationally important metals that are not routinely analyzed in the recycling industry. This could supply the occupational health professional with a semiquantitative exposure index for metals as beryllium, cadmium, chromium, lead and nickel increasing the efficiency of their exposure assessment strategies. Only metals with more than 85% of results above their respective detection limits were included in the analysis. On days were multiple lots were processed, the mean of the concentration was used. All adjusted R-square values were between -0.1 and 0.1 indicating no correlation between air and bulk samples for shredding. Concentration limits of 200 ppm for beryllium placed on incoming scrap and bullion by a North American copper smelter makes it equally interesting to compare bulk and air sample results. In the case of shredding, only one sample approached 200-ppm beryllium with a corresponding air sampling value of 0.00002 mg/m³.

V. DISCUSSION

Air sampling data showed that with existing engineering controls in place, occupational exposure to airborne metals analyzed fit the definition of “well controlled” with the exception of silver. Percent exceedance values are less than one percent and the geometric standard deviations are all less than 2.5 for metals considered to be well controlled. The source of the operator’s silver exposure is under study as the circuit boards contain little silver relative to copper or iron, where exposures were very low. Co-located processes may have contributed to the air levels measured in the shredding process and include a ring mill shredder used for processing other types of input material, roasting furnaces used to reduce the volume of the product sample. A milling operation used to reduce the size of the sample to create a more representative material for assaying was also nearby. Of the metals analyzed from the bulk samples, selenium was the only metal always below the detection limit. Greater than 50 percent of the samples for arsenic, beryllium, and cadmium were below detection limits. Correlations between air sampling and bulk sampling data were not significant for shredding.

VI. CONCLUSION

The Untha shear shredder equipped with ventilation, as is typical in the industry, represents a minimal inhalation hazard regarding silver and no inhalation hazard to the operators for all other metals studied. Attempts to correlate air sampling results with bulk sample concentrations were not successful. In order to understand the nature of exposures throughout the entire valuation process, a survey of roasting, milling, melting and casting is needed.

ACKNOWLEDGMENT

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REFERENCES