Evaporation of Mercury from CCFLs during Recycling of LCD Television Sets

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Abstract
The element mercury is one of the most hazardous substances known. Still, it is common in the air, water, soil and products we use in our daily life. LCD TVs is one of these products. To prevent the mercury in the LCD TVs from polluting the environment, the LCD TVs are recycled. This is done through automatic shredding or manual disassembly where the mercury can spread in the work environment, the process equipment or to the recycled material. This is due to broken CCFLs in the LCD TVs which contain the mercury. The aim of this paper is to investigate, through a literature review and an empirical study, the amount of mercury released into the work environment due to broken CCFLs from LCD TVs. In the literature review there were found the amount of mercury other researchers has found in CCFLs from LCD TVs, and also where the mercury was found. In the empirical study, the amount of mercury in a LCD due to broken CCFLs were measured and validates the results from other researcher and states that the mercury is difficult to predict.

Keywords:
Mercury, recycling, disassembly, liquid crystal display, television set, cold cathode fluorescent lamps.

1 INTRODUCTION

Mercury (the element) is one of the most hazardous substances in the world [1]. It is naturally present in air, water and soil [2]. It is estimated that the natural mercury emissions to the atmosphere are between 800 and 6000 tonnes annually [3-6]. Additionally, 2320 tonnes of mercury are emissions caused by man [6]. Mercury is absorbed by all living organisms and becomes more concentrated in organisms higher in the food chain, especially in aquatic animals. Humans can be exposed to mercury by eating, drinking water and breathing air. The general concentration of mercury vapours in the air is expected to be between 2-4 ng/m² in remote areas and about 10 ng/m² in urban areas [7-8].

Mercury is also present in many products. Examples of such products are thermometers, switches, pressure guards, flow meters, valves, rectifiers, thermostats, cold cathode fluorescent lamps (CCFLs), paint, dental amalgam and skin care products [4, 9-11]. CCFLs are used in several lighting applications, e.g. liquid crystal display (LCD) television sets (TVs), scanners, LCD monitors, and digital cameras [11].

The common recycling of LCD TV containing CCFLs in Europe is done through either automatic processes (shredding) or manual disassembly [12-15]. During such processes and operations the environment and the work environment are at risk of being exposed to mercury if some precautions not are taken. The automatic recycling processes contain technologies for removal of mercury vapours [12-14, 16]. If the mercury vapours amalgamate to the recycled materials or the recycling equipment itself, then the mercury degrades the material and pollutes the surrounding environment [14]. In the case of manual disassembly, personal have the risk of mercury exposure due to the possibility of treating LCD TVS with broken CCFLs inside. The CCFLs could break, for example, during transportation, preparation before disassembly and during disassembly.

1.1 Aim
The aim of this paper is to investigate the amount of mercury vapours released from broken CCFLs from LCD TVs.

1.2 Methodology
During the work presented in this paper a literature review and an empirical study were performed. This was done to investigate the amount of mercury released into the environment and the work environment due to broken CCFLs. Following the review, a study was performed to complement, verify or contradict the literature.

2 MERCURY VAPOURS – A REVIEW

If a human breathes in mercury vapours, about 80% of the vapours will be absorbed by the body via the lungs [4, 7,
17-18]. Exposures of concentrations between 15 \( \mu g/m^3 \) and 30 \( \mu g/m^3 \) during long periods of time have shown negative effects on the human health [8]. Exposure of mercury vapours with a concentration between 1 mg/m\(^2\) and 3 mg/m\(^2\) during a few hours may cause pulmonary irritation and destruction of the tissues in the lungs, and occasionally disorders in the central nervous system. Exposure during longer periods of time may cause shaking and mental disturbances. These effects are observed during long-term exposure to mercury vapours above the concentration 0.1mg/m\(^3\) [5].

According to the World Health organisation, the annual level for mercury vapour exposure is 1 \( \mu g/m^3 \) before a risk of affecting the health occurs [8]. Table 1 contains the different work environmental levels in five different countries of mercury allowed, over a period of eight hours, five days a week.

<table>
<thead>
<tr>
<th>Country</th>
<th>Organic Hg</th>
<th>Non-organic Hg</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sweden</td>
<td>0.01 mg/m(^3)</td>
<td>0.03 mg/m(^3)</td>
<td>[19]</td>
</tr>
<tr>
<td>Taiwan</td>
<td>0.01 mg/m(^3)</td>
<td>-</td>
<td>[20]</td>
</tr>
<tr>
<td>Germany</td>
<td>0.02 mg/m(^3)</td>
<td>0.02 mg/m(^3)</td>
<td>[21]</td>
</tr>
<tr>
<td>UK</td>
<td>0.02 mg/m(^3)</td>
<td>0.02 mg/m(^3)</td>
<td>[22]</td>
</tr>
<tr>
<td>Japan</td>
<td>0.025 mg/m(^3)</td>
<td>-</td>
<td>[23]</td>
</tr>
</tbody>
</table>

### 2.1 Mercury in CCFLs

The New Jersey Department of Environmental Protection states in a report published in 2004 that between 17% and 40% of the mercury is vaporised if CCFLs are broken. This is over a period of several hours, and a third of the mercury is released over the first eight hours. [24] In the literature, the amount of mercury in CCFLs varies between 0.1 mg/lamp and 10 mg/lamp [11, 14, 17, 25-26]. According to two manufactures of CCFLs used in LCD TVs the amount of mercury in the lamps is less than 3 mg/lamp [27-28]. The number of CCFLs in LCD TVs differs in the literature between 2 and 28 lamps, depending on the size and design of the TVs [13-14, 25, 29]. The designs of LCD TVs are either a design with several CCFLs directly illuminating the LCD screen from the inside [25, 30], or a design were the light from two CCFLs is guided to the screen via a light guide [31].

According to Dang et al., the highest concentration of mercury in a fluorescent lamp is located in light emitting powder [32]. Raposo et al. state that there are differences in the concentration of mercury vapours from the emitting powder depending on the age of the CCFLs [33]; the newer CCFLs have a higher concentration, while the older CCFLs have a lower one. The authors also state that this is due to the mercury in the powder from the older CCFLs being absorbed by surrounding components. McDonnell and Williams state that the highest concentration of mercury is located in the electrodes in CCFLs, and not the light emitting powder. The authors also state that due to the disagreement in the subject the entire CCFL should be considered during end-of-life treatment. [25]

Another investigation of the amount of mercury vapour released during end-of-life treatment of CCFLs in LCD monitors and LCD TVs came to the conclusion that mercury vapours have a highly volatile behaviour. During a test, 76% of the mercury was accounted for during the end-of-life shredding process. The statement of mercury losses is based on the assumption that each CCFL contains 12 mg of mercury. During the same investigation, the exposure of mercury vapours for personal performing disassembly of LCD monitors was measured. The highest concentrations were measured in the container for broken CCFLs. The other measurement points were the workplace, and in the direct surroundings of intentionally broken CCFLs, but did not show concentrations above the recommended level in the work environment. It should be added that the workplace was fitted with a suitable ventilation system. [17]

Thaler et al. found mercury in the glass of fluorescent lamps which had been used up to about 25,000 hours. The amount of mercury bound in the glass depends of the weight of the fluorescent powder and the length of time the lamps have been used. Lower weight and a longer period of time results in more mercury bound to the glass in the lamps. [34]

### 3 EMPIRICAL STUDY

The study contained three parameters which were changed during the study while measuring the mercury vapour concentration. The parameters in the study were:

- Number of broken CCFLs
- Size of the container
- Length of time the broken CCFLs were allowed to evaporate mercury into the containers

Only one parameter was changed between the measurements to make it possible to understand the parameters effect on the mercury concentration. However, this approach makes it difficult to see any synergy effects between the parameters.

#### 3.1 Equipment used

To measure the mercury vapours a gold film mercury vapour analyser called JEROME® 431-X™ was used. The instrument has a range of detection between 0.003 mg/m\(^3\) and 0.999 mg/m\(^3\) and has a resolution of 0.001 mg/m\(^3\). The precision of the device is a 5% standard derivation at 0.100 mg/m\(^3\) of mercury. The air flow through the device is 0.75 \pm 0.05 litre/min during a measurement which takes 12 seconds. [35]

The different containers used to create air-tight volumes were 14 litre, 31 litre and 72 litre containers with lids. The volumes of the containers were selected to make an even distribution of volumes during measuring. The reason for the usage of containers, and not performing the measurements directly in a room, was to be able to simulate broken CCFLs inside a LCD TV. Another reason was to investigate if there is scalability depending on the
change of volume. A direct illuminated 42 inch LCD TV with CCFLs has a volume of approximately 14.5 litres. This is calculated with a depth of 30mm and the screen ratio 16:9.

All measurements were performed in an air cabinet with a constant flow of air at a minimum of 0.56 m/s. The JEROME instrument and the 31 litre container are illustrated in Figure 1 below.

![Image: Image of the setup](image)

**Figure 1: Image of the setup**

### 3.2 Material used

The CCFLs used were gathered from several LCD TVs of different brands, years of manufacturing, designs and sizes. The dimensions of the CCFLs are illustrated in Table 2 below.

<table>
<thead>
<tr>
<th># CCFLs</th>
<th>Diameter</th>
<th>Length</th>
<th>Series</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>4mm</td>
<td>715mm</td>
<td>1-6</td>
</tr>
<tr>
<td>16</td>
<td>3mm</td>
<td>640mm</td>
<td>7</td>
</tr>
<tr>
<td>9</td>
<td>3.4mm</td>
<td>745mm</td>
<td>8 and V1</td>
</tr>
<tr>
<td>14</td>
<td>4mm</td>
<td>835mm</td>
<td>9-10</td>
</tr>
<tr>
<td>2</td>
<td>3.3mm</td>
<td>835mm</td>
<td>10</td>
</tr>
</tbody>
</table>

All lamps were collected from a discarded LCD TVs provided by a recycling centre in Linköping, Sweden. A recycling centre is where the community can hand in waste products such as chemicals as well as electronic and combustible products for future treatment, recycling or incineration. The number of hours the LCD TVs were used during their life-times is unknown.

### 3.3 Plan of the empirical study

The study was divided into 10 series, with each series representing the different setups of parameters. During Series 1-7, the influence of changing the number of broken CCFLs in a 31 litre container was investigated. Series 8-10 were performed to investigate the influence of changing the volume eight CCFLs were broken in. The additional series was performed to validate if the behaviour of mercury in this context was possible to predict.

The study was performed to span a range of measurements to support the understanding of the behaviour of the outcome in the test series. When the behaviour was assumed to be understood a hypothesis was created. To falsify or validate the hypothesis a statement was made. This statement was then investigated. The result of the investigation then falsified the hypothesis if the investigation contradicted the hypothesis, and validated the hypothesis if the outcome was in line with the hypothesis.

### 3.4 Measurement procedure

Before the study began the measurement device was calibrated and warmed up according to the device instruction manual and fitted with an extension tube. Holes were also drilled in the containers to fit the extension tube at the measurement device, and the air cabinet was cleaned. The tests were made according to the following procedure.

1. The container and the measurement instrument were placed inside the air cabinet, the extension tube of the device was fitted through the hole in the container, and the end of the tube was placed as close to the centre of the box as possible.
2. The background level of mercury in the air cabinet and container was measured and documented.
3. The CCFL or CCFLs was or were placed in the centre bottom of the container and broken carefully to try to make a uniform cross section of the fracture. The box was closed with a lid as fast as possible after the CCFLs were broken.
4. Initially 10 measurements were made and documented. The 10 measurements were repeated at 15min, 30min and in the complementing series also at 45min and 60min.
5. After all measurements were performed the CCFLs were removed from the container and storage. The container and the air cabinet were then cleaned from possible glass and other materials.

### 3.5 Uncertainties and known factors affecting the test outcome

During the study there were several uncertainties which were difficult to quantify and anticipate. The identified uncertainty was the amount of mercury in the CCFLs before the study. The following known factors affect the outcome of the study.

- The temperature in the room affects the evaporation rate for mercury [36]. Room temperature was 20-21 degree Celsius.
- The air pressure also affects the evaporation rate for mercury. The air pressure in the room was 101.3 kPa.
- The amount of air “flushing” the boxes during a single measurement was 15cl. With 10 measurements the amount becomes 150cl or 1.5 litre of air flushing the containers.

### 4 RESULTS FROM THE EMPIRICAL STUDY

#### 4.1 Results from Series 1-10

The results from the measurements conducted in Series 1-7 and 9 are illustrated in Figure 2 while the values are listed in Table 3. These series were performed to investigate the influences the number of broken CCFLs
has on the mercury vapour concentration within a 31 litre container. The results from Series 8-10 are presented in Figure 3, while the values are listed in Table 4. These series were performed to investigate the influences of different volumes of containers when 8 CCFLs were broken inside. Each pile in Figure 2 and Figure 3 together with the numbers in Table 3 and Table 4 are average values.

**Figure 2:** Results from Series 1-7 and 9. *Series 9

**Table 3:** Results from Series 1-7 and 9

<table>
<thead>
<tr>
<th>Series</th>
<th>CCFL</th>
<th>Instant</th>
<th>15min</th>
<th>30min</th>
<th>45min</th>
<th>60min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>1</td>
<td>0.013</td>
<td>0.010</td>
<td>0.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>0.043</td>
<td>0.098</td>
<td>0.103</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>8</td>
<td>0.018</td>
<td>0.096</td>
<td>0.097</td>
<td>0.099</td>
<td>0.086</td>
</tr>
<tr>
<td>7</td>
<td>16</td>
<td>0.064</td>
<td>0.210</td>
<td>0.250</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3:** Results from Series 8-10.

**Table 4:** Results from Series 8-10

<table>
<thead>
<tr>
<th>Series</th>
<th>Container</th>
<th>Instant</th>
<th>15min</th>
<th>30min</th>
<th>45min</th>
<th>60min</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>14</td>
<td>0.038</td>
<td>0.138</td>
<td>0.133</td>
<td>0.121</td>
<td>0.107</td>
</tr>
<tr>
<td>9</td>
<td>31</td>
<td>0.018</td>
<td>0.096</td>
<td>0.097</td>
<td>0.099</td>
<td>0.086</td>
</tr>
<tr>
<td>10</td>
<td>72</td>
<td>0.008</td>
<td>0.052</td>
<td>0.061</td>
<td>0.077</td>
<td>0.083</td>
</tr>
</tbody>
</table>

### 4.2 Expected results and results from the validating series

The value in the validating series was expected to be 0.022±0.005mg/m³. The calculation of the expected value is based on the measurements performed in Series 8 and 1-5 and 9. The value in Series 8 after 60 min is 0.107mg/m³. Compensating for the air flush issue, the value should be 0.230mg/m³ as illustrated in equation below.

\[
\text{Average of measured values} = \frac{\text{Compensated value}}{1 - \frac{\text{Changed air volume}}{\text{Volume of the container}}}
\]

This is the expected value for 8 lamps broken in a 14 litre container after 60 min. To recalculate the value of 1 CCFL instead of 8, the relationship between Series 1-5 and 9 can be used. The closest values with a relationship are after 30 min, with 0.010mg/m³ and 0.097mg/m³ respectively. The increase in mercury concentration when changing from 1 CCFL to 8 is 918% based on the compensated values. The same increase is assumed to be identical at 60 min. This assumption, together with the compensated value from Series 8 at 60 min gives the expected value of 0.0226±0.023mg/m³. The expected value without the air flush compensation is 0.022mg/m³. The variation of ±0.005 is based in the standard variation of the instrument. The result from the validation series is 0.058mg/m³, 163% higher than expected.

### 5 DISCUSSION

In the literature it is stated that the mercury occurrence as a vapour and amalgamated to materials. [24-25, 32-33] Mercury has not only been found in vapours from fluorescent lamps; it has also been found in the electrodes [17], in the glass [34] and in the fluorescent powder [32-33] of the lamps. This indicates that this is the case with CCFLs in LCD TVs as well. This makes it important to understand.

During the empirical study the following relationships were found. If the number of broken CCFLs increases, then the mercury concentration also increases. If the container volume increases, then the mercury concentration decreases. The highest value measured was 0.250mg/m³ for 16 broken CCFLs in a 31 litre container after 30 min. This will make the concentration even higher if 16 CCFLs is broken inside a 42 inch TV. As the expected value and the validation series illustrates, the concentration is difficult to predict as stated by Böni and Widmer [17]. The expected value was not the same as the validating value which clearly states that the behaviour of mercury in CCFLs from LCD TV s is not fully understand. The validation series also illustrates that the
concentration of mercury caused by a single broken CCFLs in a 42 inch TV can be 0.058mg/m³ after accumulation over one hour.

What to prefer for statistic validation, many measurement in few CCFLs or few measurements on many CCFLs? The drawback with our selected approach was the issue of air flushing the sample volume each time a measurement was performed. Why did we select this approach? This is due to the limitation of the number of CCFLs and the variation due the unpredictable nature of mercury. The reason for not breaking more than 16 CCFLs in a container was the high concentrations measured and that JEROME device was saturated and had to be regenerated after a few measurements with more than 16 CCFLs.

6 CONCLUSION

The literature reviews showed that not only does the fluorescent powder in CCFLs in LCD TVs contain mercury; in fact the entire CCFL, especially older and used CCFLs, have mercury amalgamated to the glass and the electrodes as well [25, 32-34]. The amount of mercury in CCFLs varies in the literature from 0.1mg to 10mg per lamp [11, 14, 17, 25-26]. The empirical study revealed the difficulty in trying to predict the concentration if one or several CCFLs are broken inside a container. The highest concentration measured, 0.250mg/m³, was for 16 CCFLs broken inside a 31 litre container measured after 30 min. The concentration measured for a single CCFL, broken in a 14 litre container representing a direct illuminated 42-inch LCD TV, was 0.058mg/m³ when measured after 60 min. If a higher number of CCFLs are broken in a LCD TV, then the mercury concentration can be expected to be higher.

7 FUTURE RESEARCH

Ideas for future research are to complement the empirical study and mathematical describing the relationship of broken CCFLs, container and the concentrations of mercury.

8 ACKNOWLEDGMENTS

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