The location and character of mercury in waste LCD backlights

A report that summarises research into mercury in end-of-life LCD televisions and monitors, which is found in the lamps used to illuminate this equipment. The report is intended to inform decisions on how best to handle waste LCD equipment at treatment facilities.
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We work with businesses and individuals to help them reap the benefits of reducing waste, develop sustainable products and use resources in an efficient way.

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Executive summary

LCD televisions and monitors typically use cold cathode fluorescent lamps (CCFLs) to illuminate the screen. Most CCFLs contain mercury, and therefore questions arise as to the best way to handle LCD equipment at the end of its life. In addition, this equipment is subject to minimum treatment standards under the Waste Electrical and Electronic Equipment WEEE Directive; Defra’s guidance on Best Available Treatment Recovery and Recycling Techniques (BATRRT), which implements WEEE treatment standards, requires certain mercury containing components, including CCFLs, to be removed whole during treatment. Additionally, employers have a legal obligation under Control of Substances Hazardous to Health (COSHH) to carry out their own suitable and sufficient risk assessments and to implement effective controls to prevent or control exposure of employees to hazardous substances, such as mercury.

The focus of this study was to investigate the location and character of mercury in the back lights of end-of-life LCD equipment. It did not aim to quantify the amounts of mercury which has been the subject of other studies. The findings of this study are intended to contribute to developing suitable treatment practices and is focused on building knowledge that will be of use to the WEEE treatment industry in assessing risks and implementing effective controls to prevent or control emissions of mercury to the environment and exposure to employees.

This report does not address how the identified mercury forms should be managed but does highlight some potential hazards which should be considered by recyclers when developing risk assessments. Further information on COSHH and management techniques is available from www.hse.gov.uk/coshh

The number of CCFLs in LCD televisions can vary between two and 22, and each contains a small amount of mercury in order to create a vapour discharge. During the equipment’s working life, the available mercury is gradually depleted, and takes different forms elsewhere inside of the CCFL.

Researchers recovered a selection of CCFLs from LCD equipment arriving at a recycling facility. They then analysed them to identify the location of the mercury within the components of each lamp. Analysis was performed on a sample of the electrodes, fluorescent powder and deposits on the glass adjacent to the electrodes. Some electrodes were made of nickel, and others of molybdenum.

The researchers used the following techniques: Hydrochloric Acid washing; Scanning Electron Microscopy (SEM); Energy Dispersive X-Ray Spectroscopy (EDS); Cold Vapour Atomic Absorption Spectroanalysis (CVAAS); Thermogravimetric Analysis (TGA); and Mercury Vapour Analysis (MVI).

Both elemental mercury and compound mercury (bound to internal components), were found inside sample CCFLs. Each of these may require different handling techniques. Analysis found that mercury was distributed on nickel electrodes as droplets, as compared to a strong surface distribution of mercury on molybdenum electrodes.

It is clear that elemental mercury was present in the used CCFLs, and was found in droplets ranging from 10μm to 500μm in diameter. The larger mercury droplets on the nickel

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electrodes had a coating that prevented their vaporising. Smaller mercury droplets were encased in debris on the electrode and encrusted in fluorescent powder adjacent to the electrode. Burnt fluorescent powder on the glass tube wall was found to contain mercury, suggesting that mercury droplets were encased in the burnt powder.

The mobility of these droplets when a lamp is broken suggests a risk of contaminating the surrounding environment. This could present an inhalation risk for handlers of broken CCFLs without adequate protective control measures. The suggested longevity of mercury droplets, believed to result from their being coated with debris, could also present an accumulating contamination risk for the working environment.

Previous research and the findings of this work suggest that it is difficult to recover and demonstrate recovery of the mercury from shredded flat panel displays. It is important to be able to demonstrate recovery and the practices in place to protect the workforce and environment.

This study implies that an automated shredding process would require a suitable mercury abatement system to prevent mercury becoming airborne in the wider environment. The mercury locked in CCFL components would not be readily detectable by random sampling of shredded material. Without suitable processes to isolate mercury after shredding, the shredded material would be classed as hazardous.

Further investigation would be required to understand the fate of mercury released from CCFLs during a shredding process.
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<td><strong>Backlight</strong></td>
<td>a lamp for illumination used in LCD screens as LCDs do not produce light themselves</td>
</tr>
<tr>
<td><strong>CCFL</strong></td>
<td>a type of fluorescent lamp typically used as a backlight</td>
</tr>
<tr>
<td><strong>Cold Cathode Fluorescent Lamp</strong></td>
<td></td>
</tr>
<tr>
<td><strong>CVAAS</strong></td>
<td>a technique used in the measurement of trace amounts of volatile heavy metals such as mercury</td>
</tr>
<tr>
<td>**Cold Vapour Atomic Absorption</td>
<td></td>
</tr>
<tr>
<td><strong>Spectroanalysis</strong></td>
<td></td>
</tr>
<tr>
<td><strong>EDS</strong></td>
<td>a technique used to analyse the elemental or chemical character of a sample</td>
</tr>
<tr>
<td><strong>Energy Dispersive X-Ray</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Spectroscopy</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Electrode</strong></td>
<td>an electrical conductor used to make contact with a non-metallic part of a circuit</td>
</tr>
<tr>
<td><strong>elemental mercury</strong></td>
<td>mercury as a pure chemical element</td>
</tr>
<tr>
<td><strong>LCD</strong></td>
<td>a thin, flat electronic visual display that uses the light modulating properties of liquid crystals, while not directly emitting light themselves</td>
</tr>
<tr>
<td><strong>Liquid Crystal Display</strong></td>
<td></td>
</tr>
<tr>
<td><strong>mercury compound</strong></td>
<td>mercury bound with other chemical elements</td>
</tr>
<tr>
<td><strong>μm</strong></td>
<td>one-millionth of a metre</td>
</tr>
<tr>
<td><strong>micrometre or micron</strong></td>
<td></td>
</tr>
<tr>
<td><strong>MVI</strong></td>
<td>a mercury vapour indicator to analyse exhaust gas for its mercury content</td>
</tr>
<tr>
<td><strong>Pyrolysis</strong></td>
<td>decomposition of a substance at high temperature in the absence of oxygen</td>
</tr>
<tr>
<td><strong>RoHS Directive</strong></td>
<td>European Community directive 2002/95/EC banning the placing on the EU market of new electrical and electronic equipment containing more than agreed levels of mercury and other materials</td>
</tr>
<tr>
<td><strong>Restriction of Hazardous Substances</strong></td>
<td></td>
</tr>
<tr>
<td><strong>SEM</strong></td>
<td>a technique using an electron microscope that provides images of a sample surface by scanning it with a high energy beam of electrons</td>
</tr>
<tr>
<td><strong>Scanning Electron Microscopy</strong></td>
<td></td>
</tr>
<tr>
<td><strong>TGA</strong></td>
<td>a technique to determine change in weight in relation to change in temperature</td>
</tr>
<tr>
<td><strong>Thermogravimetric Analysis</strong></td>
<td></td>
</tr>
<tr>
<td><strong>WEEE</strong></td>
<td>electrical and electronic goods that have been discarded by the final user</td>
</tr>
<tr>
<td><strong>Waste Electrical and Electronic Equipment</strong></td>
<td></td>
</tr>
<tr>
<td><strong>WEEE Directive</strong></td>
<td>European Community directive 2002/96/EC setting collection, recycling and recovery targets for many types of electrical goods</td>
</tr>
<tr>
<td><strong>XRD</strong></td>
<td>a technique used to characterise the structure, size and preferred orientation of crystals in a sample, commonly used to identify substances</td>
</tr>
</tbody>
</table>
1.0 Background and Objectives

1.1 Background

Changes in technology mean that cathode ray tube televisions and monitors are no longer sold in the UK. LCD (Liquid Crystal Display) technology has come to dominate the market, and this equipment is now starting to enter the waste stream as it reaches the end of its life. Arisings of waste LCD equipment can be expected to grow over the coming years, with peak arisings anticipated in the next three to five years.

<table>
<thead>
<tr>
<th>Year</th>
<th>2013</th>
<th>2014</th>
<th>2015</th>
<th>2016</th>
<th>2017</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tonnes</td>
<td>70,000</td>
<td>100,000</td>
<td>115,000</td>
<td>120,000</td>
<td>115,000</td>
</tr>
</tbody>
</table>

This has implications for treatment facilities handling WEEE (Waste Electrical and Electronic Equipment), as LCD equipment contains components that are classed as hazardous and that need to be handled appropriately at the treatment stage. This study concerns the component most LCD units use to illuminate the screen – the CCFL (Cold Cathode Fluorescent Lamp). These are also known as backlights. CCFLs contain a small amount of mercury, a metal with toxic properties.

The WEEE Directive requires the mercury in CCFLs to be removed and recovered. This poses particular challenges during treatment, as facilities need to dismantle LCD equipment safely and effectively, but also in a cost efficient way. The volatile nature of mercury, its ability to take other forms such as amalgams, and the requirement for removal during processing, present questions of mercury containment for both manual and automated disassembly.

Treatment facilities need methods which can be audited to show that mercury has been removed from the waste stream, and not lost through mixing into a larger volume of shred material.

1.2 Objectives

This study seeks to fill gaps in knowledge of how to deal effectively with the mercury contained in CCFLs in waste LCD equipment. These include establishing the quantities of mercury they contain, including any mercury compounds formed during the operation of the equipment, and the location of these materials.

This report is primarily aimed at operators of WEEE collection and treatment operators and facilities who wish to understand the issue in greater detail.
2.0 CCFLs and how they work

2.1 Structure

The majority of LCD televisions and monitors are fitted with CCFLs. They perform the function of illuminating the LCD screen. They are long thin fluorescent glass tubes of between two and four millimetres in diameter, connected electrically by wire-ended electrodes that are sealed at the ends of the tube. Figure 1 shows a diagram of a typical CCFL.

![Diagram of a typical CCFL used in LCD equipment](image1)

Figure 1 Diagram of a typical CCFL used in LCD equipment

The tube of a CCFL is made of borosilicate glass with a tri-phosphor coating lining the internal wall. The standard electrodes used in CCFLs are cylindrical in design with a lead wire linking the electrode to the outside of the tube through an opening which has been hermetically sealed. A mercury reservoir is placed on the inside of the tube, which is filled with penning gases (argon and neon).

During operation an electronic inverter supplies high voltage AC electricity across the electrodes, the penning gases conduct current, and the elemental mercury is activated to form a vapour. The release of the energy in the vapour results in an ultraviolet discharge which stimulates the phosphor coating to produce a visible source of light. A diagram of the operation of a CCFL is illustrated in Figure 2.

![Diagram of a CCFL in operation](image2)

Figure 2 Diagram of a CCFL in operation

2.2 The role of mercury

Each CCFL contains a small amount of mercury in order to create a vapour discharge. The lamp manufacturers have declared an average amount of mercury per lamp as being 3.5mg, which is similar in size to the roller ball found in a ball point pen. During the working life of a CCFL, the mercury available in the reservoir for discharge is depleted. While it has been suggested that the mercury is deposited onto the fluorescent powder coating, this study investigates the location of the depleted mercury more closely.
2.3 Application

The number of CCFLs in an LCD unit varies between two and 22. The method by which CCFLs illuminate the LCD differs between computer monitors and televisions. Televisions have an array of CCFLs mounted directly behind the LCD screen, while monitors have CCFLs fitted into metal carriers at the top and bottom of the screen. Televisions typically contain a higher number of CCFLs compared to monitors, and the larger the screen, the greater the number of CCFLs fitted.

CCFLs are typically attached to the LCD unit by one of four different ways: by printed circuit boards; by dual connectors; by a single connector and a circuit board; or as a single u-tube and connector. These are illustrated in Figure 3 below.

![Figure 3](image)

**Figure 3** Typical configurations of CCFLs in LCD televisions

2.4 Environmental hazards

Mercury is a danger to human health and the environment as it has bio-accumulative properties. Humans can absorb mercury in its many forms; the respiratory and gastrointestinal tracts are considered the main receptors, although the skin can also be at risk. The nervous system is the most vulnerable organ to mercury poisoning.

The main sources of mercury exposure to humans are those resulting from occupational activities, such as product processing or mercury-bearing waste collection, storage and treatment. Regulatory occupations exposure limits are in force to provide protection for workers involved with mercury. Research has concluded that mercury release from broken compact fluorescent lamps in confined conditions could pose an environmental health hazard.

Mercury released from a broken fluorescent lamp may be in the form of vapour or compounds. It may also be bound with components within the lamp.
3.0 Tests completed to understand mercury in CCFLs

3.1 Introduction

The researchers recovered a selection of CCFLs from LCD equipment arriving at a recycling facility. They then analysed the lamps to identify the location of the mercury within the components of each lamp. Analysis was performed on samples of the:

- electrodes;
- fluorescent powder; and
- deposits on the glass adjacent to the electrodes.

Some sample electrodes were constructed of nickel, and others of molybdenum.

3.2 Methods of analysis

The researchers used the following techniques: Hydrochloric Acid washing; Scanning Electron Microscopy (SEM); Energy Dispersive X-Ray Spectroscopy (EDS); Cold Vapour Atomic Absorption Spectroanalysis (CVAAS); Thermogravimetric Analysis (TGA); and Mercury Vapour Analysis (MVI).

These are expanded upon in Figure 4, with the rationale for each test. Appendix III contains full details of the tests undertaken.

<table>
<thead>
<tr>
<th>Test</th>
<th>Test (short title)</th>
<th>Reason for test</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Hydrochloric Acid Washing</td>
<td>HCl washing</td>
<td>To determine the amount of elemental mercury in a sample</td>
</tr>
<tr>
<td>2. Pyrolysis with Cold Vapour Atomic Absorption Spectroanalysis</td>
<td>Pyrolysis with CVAAS</td>
<td>To determine the amount of mercury in all its forms (elemental and compound) in a sample</td>
</tr>
<tr>
<td>3. X-ray Diffraction Analysis</td>
<td>XRD</td>
<td>To investigate the structure of a sample and the possibility of mercury absorption</td>
</tr>
<tr>
<td>4. Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy Analysis</td>
<td>SEM with EDS</td>
<td>To visually identify mercury deposits on a sample, and to confirm their composition</td>
</tr>
<tr>
<td>5. Thermogravimetric Analysis with Mercury Vapour Indicator Analysis</td>
<td>TGA with MVI</td>
<td>To determine whether mercury is present in a sample, and if so, the temperature at which it is vaporised</td>
</tr>
</tbody>
</table>

**Figure 4 List of tests**

CCFL samples were subjected to tests as a whole by breaking open the tube in a controlled manner, and the individual components were also subjected to tests, by separating and storing them, again in a controlled way. Further details about these procedures can be found in Appendix II.

Each of the tests listed in Figure 4 can be explained in further detail:

**3.2.1 HCl washing**

HCl washing is used to measure the amount of elemental mercury in a sample. Each sample was immersed and washed in hydrochloric acid, and then removed. This removed the mercury from the sample and kept it suspended in the acid solution. A pre-weighed gold evaporation slug was introduced into the solution, which was then warmed to 60°C, swirling the contents to ensure the gold moved through the solution. After five minutes the gold slug was removed and washed with de-ionised water, and then immersed in acetone. The slug was removed once more, whereupon the
acetone evaporated. The gold slug was then weighed to determine the weight of the mercury removed from the sample.

This was performed for the complete CCFL interior and for pairs of electrodes removed from the CCFL. A method to wash and agitate electrode pairs using hydrochloric acid was used, to establish whether both elemental and bonded mercury were present. The washing process detached elemental mercury from the surface of the electrodes. The washed electrodes were then inspected using SEM along with EDS. TGA analysis was then carried out to establish whether mercury continued to be present on the washed electrodes.

3.2.2 Pyrolysis with CVAAS

Pyrolysis of individual components from waste CCFLs, followed by CVAAS, was undertaken to quantify their mercury content.

The components were:
- Glass tube
- Fluorescent powder
- Electrodes
- Elemental mercury

The samples were subject to pyrolysis in a furnace operating at 550°C, resulting in the desorption of any mercury present. The mercury vapour was then drawn through a detection cell, and the vapour concentration was measured by the CVAAS unit.

3.2.3 XRD

Samples of fluorescent powder were analysed using XRD to investigate their structure and the possibility of mercury absorption. The samples were:
- virgin powder;
- used powder recovered from waste CCFLs; and
- powder from an unused CCFL.

3.2.4 SEM with EDS

Sample electrodes from CCFLs were analysed using SEM to visually identify mercury deposits on each electrode, and then subjected to EDS to confirm the composition of the deposits.

Two types of CCFL were used as samples for analysis using SEM with EDS:
- one with nickel electrodes; and
- another with electrodes made of molybdenum.

Electrode samples were mounted onto self-adhesive carbon pads. Electrodes from each CCFL were retained in pairs to determine any variation between them. The electrodes were not removed from their glass surround, but exposed with part of the glass and phosphor powder adjacent.

Pairs of electrodes from each sample were subjected to SEM analysis, to determine visually whether they showed variation in ageing, corrosion or deposition.

EDS analysis was used to confirm that droplets identified through SEM were composed of mercury.

In order to investigate powder found in the samples, a process of gold coating was used to provide greater detail when subjected to SEM. This would reveal a better surface topography of the components and materials around the electrode area of the CCFL.

The researchers carried out further SEM analysis of electrodes to investigate the presence of mercury amalgamated with the metal structure of the electrode. They also froze the CCFL samples during the sectioning process to reduce the likelihood of mercury inadvertently being dislodged.

3.2.5 TGA with MVI

The aim of using TGA on the electrodes and fluorescent powder from CCFLs was to determine, (a) whether mercury was present in these materials, and if so (b) the temperatures at which the mercury was liberated from the samples.
The samples were:

- control samples to verify equipment operation;
- fluorescent powder from spent and unused lamps; and
- electrodes made of nickel and molybdenum.

The test involved the use of thermal desorption pans in a nitrogen gas flow atmosphere. The temperature rise of the desorption chamber was set at a 10°C rise per minute to achieve a final temperature of 550°C. A holding temperature of 550°C was set for 10 minutes. The weight of the sample was correlated to time and temperature.

The exhaust gas from the electrode samples was analysed for mercury content using an MVI.

The electrode samples subjected to TGA were further examined using SEM to determine whether TGA had affected the surface.
### 4.0 What was found

<table>
<thead>
<tr>
<th>Test (short title)</th>
<th>Reason for test</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. HCl washing</td>
<td>To determine the amount of elemental mercury in a sample</td>
<td>0.1mg to 1.4mg elemental mercury present per CCFL</td>
</tr>
<tr>
<td>2. Pyrolysis with CVAAS</td>
<td>To determine the amount of mercury in all its forms (elemental and compound) in a sample</td>
<td>Mercury found in both electrodes and fluorescent powder. Even when subject to HCl washing, mercury remained bonded to or enclosed in the electrode</td>
</tr>
<tr>
<td>3. XRD</td>
<td>To investigate the structure of a sample and the possibility of mercury absorption</td>
<td>Inconclusive</td>
</tr>
<tr>
<td>4. SEM with EDS</td>
<td>To visually identify mercury deposits on a sample, and to confirm their composition</td>
<td>Mercury droplets found attached to electrodes and glass fragments around electrodes, and encrusted with fluorescent powder. Droplet coating could delay evaporation</td>
</tr>
<tr>
<td>5. TGA with MVI</td>
<td>To determine whether mercury is present in a sample, and if so, the temperature at which it is liberated</td>
<td>Analysis of fluorescent powder was inconclusive. Mercury was found to be present on electrodes. Lesions on the electrodes could harbour mercury</td>
</tr>
</tbody>
</table>

**Figure 5** List of tests and results

### 4.1 Results from HCL washing

This test showed that elemental mercury was present in CCFLs recovered from waste LCD equipment, ranging from 0.1mg to 1.4mg by weight per CCFL.

The washed electrodes were inspected using SEM along with EDS. TGA analysis was then carried out to establish whether mercury continued to be present on the washed electrodes. The TGA analysis showed that even though mercury had been agitated from the surface of the electrode, there was a weight loss between 100°C and 300°C. This suggested that both elemental and compound (bonded) mercury were present on the electrode.

### 4.2 Results from Pyrolysis with CVAAS

Analysis of the fluorescent powder and the electrodes from used CCFLs revealed sharp rises in detected mercury vapour as the sample was heated. Mercury was therefore present in both materials.

The multiple sample analysis of the fluorescent powder produced a range of concentrations normally distributed around a mean of 2328 ppm of mercury. While it was not possible to determine whether there was a gradient of mercury concentration in the tube wall powder along its length, it is reasonable to suggest that concentrations of mercury in the powder would be higher towards the dominant electrode.

CVAAS analysis of the electrode showed significantly higher concentrations of mercury deposited on or in the electrode surface. The highest concentration was 19600 ppm of mercury on the leading edge of
the electrode assembly. Lower concentrations were found towards the rear of the electrode. This is shown in Figure 6.

![Figure 6: Mercury concentration along sections of electrode](image)

The analysis therefore suggests that mercury is concentrated toward the leading edge of the electrode. Even when the sample electrodes were treated in an HCl wash, CVAAS analysis showed mercury to be bonded to or enclosed in the surface of the electrode. Therefore mercury could be encased by deposits forming on the leading edge of the electrode and covering lesions in the surface.

### 4.3 Results from XRD

This analysis was inconclusive. To assess accurately whether mercury in CCFLs affects the lattice structure of the fluorescent powder, further repeated analysis of CCFLs from a similar batch of LCD equipment would be needed.

### 4.4 Results from SEM with EDS

This analysis found mercury droplets of various sizes on electrodes and fluorescent powder. These droplets were:

- attached to the electrode body;
- attached to the glass fragments surrounding the electrode;
- free released on breakage of the tube; and
- encrusted with fluorescent powder residue, possibly released from the discoloured powder adjacent to the electrode.

While the presence of elemental mercury was confirmed, the presence of compound mercury was not confirmed.

The preparation of the CCFL samples, as detailed in Appendix II, resulted in mercury droplets being released into the large Petri dish. This occurred on breakage of the CCFL close to the point where the electrode was sealed into the glass tube. Breakage elsewhere in the glass tube showed no visual signs of mercury release.

Mercury droplets were found attached to the surface of nickel electrodes and the glass edge of the tube wall. Researchers estimated that these droplets had diameters of 70μm and 110μm respectively.
They also visually identified smaller droplets. EDS analysis confirmed the droplets contained nickel and mercury.

The mercury droplets found on the edge of the tube wall showed accumulation of surface debris. It is unclear how this occurred. Figure 7 shows a mercury droplet on the glass wall of the CCFL adjacent to the electrode. Figure 8 shows a mercury droplet with fluorescent powder covering a significant part of the surface. Its origin within the CCFL is unknown.

![Figure 7](image1.png)

**Figure 7** Mercury droplet on glass wall adjacent to electrode

![Figure 8](image2.png)

**Figure 8** Mercury droplet released from CCFL
The gold coating technique revealed better detail of the electrode components and the materials around them. A mercury droplet on the electrode measuring about 12 μm was studied and found to be encrusted with fluorescent powder. This is shown in Figure 9. Researchers established that small droplets of mercury could lie buried in the discoloured structure of the fluorescent powder of the CCFL.

![Encrusted mercury droplet on surface of sample electrode](image)

**Figure 9** Encrusted mercury droplet on surface of sample electrode

Analysis showed that pairs of nickel electrodes typically had one electrode with heavy deposits of mercury droplets, and the other with few deposits. Over time, one half of the electrode pair hosts more mercury than the other.

Molybdenum electrodes, while showing little evidence of mercury droplets, nonetheless had a strong surface distribution of mercury.

Researchers were interested to observe that a mercury droplet being studied remained intact for a twelve-week period without any significant changes in its diameter or formation. EDS analysis showed it to contain aluminium and oxygen in addition to mercury. This suggested that the surface coating could be providing a barrier for mercury evaporation.

One sample CCFL was found to have a larger diameter sphere of mercury (500 μm), suggesting that it retained a significant working reservoir of mercury.

Comparative analysis of used fluorescent powder and virgin powder was carried out. Fluorescent powder from the glass wall of the CCFL showed a strong signature for mercury, together with evidence of nickel when subjected to EDS.

### 4.5 Results from TGA with MVI

Analysis of spent fluorescent powder as compared to virgin powder was inconclusive, and could not demonstrate the presence of mercury in the body of the powder. Due to the small quantities and difficulty in removing burnt fluorescent powder adjacent to the electrode, it was not possible to collect a sufficient sample for analysis. It is, however, suggested that mercury droplets were present on the surface or encased in the burnt powder adjacent to the electrodes.

The electrodes exhibited significant weight loss during TGA in the temperature range from 70°C to 275°C. Monitoring of the exhaust gas with MVI showed that mercury vapour was released through the TGA process. The MVI showed mercury concentrations up to 400 μg/m³. Analysis of electrode pairs revealed that one of each pair was the primary source of mercury vapour.
It was unclear whether the mercury was simply attached to the surface of the electrode, or also lay within the electrode. The electrode subjected to TGA was then further examined using SEM to help answer this. It showed lesions in the surface of the electrode, which may have been revealed during the TGA vaporisation process. Mercury could be present in these lesions encased in the build-up of displaced fluorescent powder.
5.0 The implications of what was found

This work was carried out to help better understand the location of mercury within CCFL containing screens to allow for their appropriate management and treatment when they reach end of life. This knowledge and information is of interest and importance to treatment operators where they are handling CCFL containing screens on a regular basis.

Both elemental mercury and compound mercury, bound to internal components, were found inside sample CCFLs. Significant total amounts of mercury, up to 3.88mg per CCFL, were found.

It is clear from this research that the areas of highest mercury concentration in waste CCFLs were the electrodes. The fluorescent powder from spent CCFLs showed a lower concentration of mercury and this was therefore the secondary source of mercury contamination. These findings run contrary to previous research results\(^2\), which suggested that fluorescent powder harboured the majority of the mercury. Therefore appropriate recovery methods are required for each of the forms.

This investigation has shown that breakage of CCFL tubes during handling or disassembly of LCD equipment will release mercury to the environment. The collection, transport and dismantling of damaged equipment with broken tubes therefore presents a mercury exposure risk that needs to be managed by WEEE treatment industry.

Results suggested that, on breakage of CCFL tubes, not all mercury droplets immediately vaporise. This was because the larger mercury droplets found on nickel electrodes had a coating that prevented their immediate vaporisation, while the smaller droplets were encrusted in fluorescent powder adjacent to the electrode. Significant amounts of mercury were identified even after the components were washed.

The small size of some of the measured mercury droplets (PM10) will mean that some droplets will be respirable. The mobility and suggested longevity of the droplets are also a potential source of workplace contamination.

The research suggests that the even with the use of local extraction venting the likelihood of contamination of dismantling workstations by larger mercury droplets is possible.

Analysis has shown that mercury on the surface of exposed electrodes quickly starts to vaporise as the temperature passes 100°C. The temperature required to release mercury from the electrodes was high to allow for understanding of mercury content. These temperatures are unlikely to be reached within the work place. However, while the rate of vaporisation at lower temperatures, such as 40 to 50°C, is unclear, the possibility of vaporisation may have implications for those working around storage containers holding broken CCFLs.

The different forms of mercury found in waste CCFLs represent both immediate and long-term sources of exposure, to collection and treatment operators as listed in Figure 10. It is possible to control or mitigate these hazards through implementation of a range of controls. For further information on COSHH please visit http://www.hse.gov.uk/coshh/

<table>
<thead>
<tr>
<th></th>
<th>Immediate hazard</th>
<th>Longer term hazard</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vapour</td>
<td>Inhalation</td>
<td></td>
</tr>
<tr>
<td>Uncoated droplets of mercury</td>
<td>Inhalation</td>
<td>Skin exposure</td>
</tr>
<tr>
<td></td>
<td>Droplets disperse and settle on surrounding surfaces, evaporating over time.</td>
<td>Build up of mercury on surrounding surfaces. Potentially, mercury forming</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Location</th>
<th>Character of Mercury</th>
<th>Method of Exposure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coated drops of mercury</td>
<td>Contamination of flat panel material streams.</td>
<td>Inhalation</td>
<td>Droplets disperse and settle on surrounding surfaces, do not evaporate. Potential to release this mercury through shear force (wiping, sliding of materials).</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Skin exposure</td>
<td>Build up of mercury droplets encased in phosphorous on surrounding surfaces. Potentially, this casing is removed as the droplets are disturbed and the mercury will form amalgams with surface, which may inhibit the ability to remove it.</td>
</tr>
<tr>
<td>Amalgam with electrodes</td>
<td>No risk highlighted as mercury locked in as amalgam</td>
<td>Possibly skin exposure risk if handled directly</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 10** Exposure risks for recycling operatives to mercury when recycling LCD screens

From the perspective of manual recycling, BATRRT requires the removal of the complete CCFL tube intact for further treatment. Where the CCFL breaks during dismantling, the transfer of mercury droplets to hands, clothes and the wider environment is possible. Materials extracted from CCFLs for recycling, if stored outdoors, could leach mercury into water drainage systems.

Automated disassembly by shredding would be likely to distribute mercury droplets, and mercury containing components, across the shred and shredder environment. An automated shredding process would require a suitable mercury abatement system to prevent mercury becoming airborne in the wider environment.

The mercury locked in CCFL components would not be readily detectable by random sampling of shredded material. Without suitable processes to isolate mercury after shredding, the shredded material would be classed as hazardous. It is suggested that investigation will be needed to understand the fate of mercury released from CCFLs during a shredding process.
Appendix I – Literature Review

A. Quantities of mercury in CCFL

Previous research to determine the quantity of mercury contained in CCFLs has proved to be inconclusive. It is suggested that there has been no standard dose of elemental mercury introduced into tubular fluorescent lamps, although manufacturers are striving to reduce the amounts.

Under the 2002 EU RoHS directive, the amounts of mercury allowable in CCFLs used in special applications was not defined. However the re-cast of the RoHS directive under consideration in 2010 expands the categories of defined fluorescent lamps. Permitted quantities of mercury in CCFLs used in LCD applications have been set dependent on tube length and size.

The amounts of mercury that can be used are to be reduced on a prescribed timescale. These new limits were agreed by the RoHS Technical Advisory Committee in May 2010 and are expected to be included in the new RoHS Directive.

Difficulties in dosing lamps with repeatable amounts of elemental mercury have shown that different batches of the similar lamp production will vary in their mercury composition. LCD equipment manufacturers have been quoted as stating that the quantity of mercury contained in CCFLs is less than 5mg per tube.

Research by the California Department of Toxic Substances Control in 2004, in which 15 different LCD devices were tested, determined the mercury content of CCFLs to range between 32 and 660mg/kg. Similar research found that the average mercury content of CCFLs ranged from 391 to 546mg/kg. This illustrates the difficulties researchers have experienced in producing similar results in the measurement of mercury contained in CCFL.

The preparation of homogeneous samples has also proved to be problematic, due to:

- the absorption of mercury by the fluorescent powder;
- formation of mercuric compounds; and
- amalgamation with alkali metals on the electrodes.

B. Content of LCD equipment relating to CCFLs

In the last decade there has been a rapid increase in the use of LCD devices, and it is estimated that 90% of all current LCD equipment uses a backlight unit. To date the majority of backlight units sold in LCD have used CCFLs as their lightsource. The number and size of CCFLs in each unit varies with the size and type of LCD screen, as shown in Figure 11.

<table>
<thead>
<tr>
<th>Type</th>
<th>Screen size</th>
<th>Average Lamp Length mm</th>
<th>Average Lamp Width mm</th>
<th>Average Lamp Weight kg</th>
<th>Number of Lamps</th>
<th>Mercury Content mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCD Monitor</td>
<td>15&quot;</td>
<td>320</td>
<td>2</td>
<td>0.004</td>
<td>2</td>
<td>7</td>
</tr>
<tr>
<td>LCD Monitor</td>
<td>17&quot;</td>
<td>350</td>
<td>2</td>
<td>0.006</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>LCD Monitor</td>
<td>19&quot;</td>
<td>390</td>
<td>2.5</td>
<td>0.006</td>
<td>4</td>
<td>14</td>
</tr>
<tr>
<td>LCD Television</td>
<td>20&quot;</td>
<td>430</td>
<td>2.5</td>
<td>0.009</td>
<td>6</td>
<td>21</td>
</tr>
<tr>
<td>LCD Television</td>
<td>26&quot;</td>
<td>630</td>
<td>3</td>
<td>0.072</td>
<td>13</td>
<td>45.5</td>
</tr>
<tr>
<td>LCD Television</td>
<td>32-37&quot;</td>
<td>805</td>
<td>4</td>
<td>0.115</td>
<td>16</td>
<td>56</td>
</tr>
<tr>
<td>LCD Television</td>
<td>42&quot;</td>
<td>920</td>
<td>3</td>
<td>0.17</td>
<td>18</td>
<td>63</td>
</tr>
</tbody>
</table>

*Figure 11 Characterisation of backlights in LCD*
Some manufacturers such as LG Philips of Korea have used a variation in external electrode fluorescent lamps. The latest generation of LCD equipment has seen LCD manufacturers replacing CCFLs with mercury-free light emitting diode (LED) backlights. The move to LED backlighting is gathering pace, with companies such as Sharp Electronics of Japan aiming to have all their high definition LCD televisions LED backlit by 2012.

From an end-of-life perspective, an LCD panel fitted with LED backlights would therefore be non-hazardous, according to a recent LCD recycling briefing note released by the UK Environment Agency. However a large volume of LCD units sold with CCFL backlights is working its way to end-of-life treatment at recycling facilities. While the Environment Agency has produced guidance confirming that electronic display devices containing mercury should be classed as hazardous, the lack of information on LCD composition and hazardous components, such as mercury in CCFLs, has been highlighted as important by WEEE recyclers.

Research has shown that the construction of a typical 37” LCD television is organised around the LCD panel, and is made up of the following components:

- Front decorative frame
- Back panel providing the enclosure for the LCD panel
- Speakers
- Electronic control boards
- Power supply (where applicable)

The LCD screen panel is a self-contained unit fitted with all the necessary electronics. The complete LCD monitor or television can therefore be conveniently divided into two areas: the LCD panel; and support components.

For a typical 37” television the bulk of the material is steel and plastic, with backlights forming 1.2% of the overall weight. A breakdown of components contained in a typical LCD television is shown in Figure 12.

<table>
<thead>
<tr>
<th>Support components</th>
<th>LCD Panel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Internal Steel</td>
<td>Steel frame &amp; back</td>
</tr>
<tr>
<td>Plastics ABS</td>
<td>Plastics</td>
</tr>
<tr>
<td>Electronics</td>
<td>LC glass &amp; electronics</td>
</tr>
<tr>
<td>Cables</td>
<td>CCFL tubes</td>
</tr>
<tr>
<td>Others</td>
<td>Cables &amp; others</td>
</tr>
<tr>
<td>Total for components</td>
<td>Total for LCD</td>
</tr>
<tr>
<td>4.94 kg</td>
<td>6.07 kg</td>
</tr>
<tr>
<td>3.40 kg</td>
<td>1.57 kg</td>
</tr>
<tr>
<td>1.47 kg</td>
<td>1.95 kg</td>
</tr>
<tr>
<td>0.28 kg</td>
<td>0.24 kg</td>
</tr>
<tr>
<td>0.33 kg</td>
<td>0.41 kg</td>
</tr>
<tr>
<td>10.42 kg</td>
<td>10.24 kg</td>
</tr>
</tbody>
</table>

**Figure 12** Composition of a typical 37” screen size LCD television

The design configuration of CCFL backlights differs between LCD monitors and televisions. In most LCD monitors the CCFLs are arranged in metal carriers fitted at the top and bottom of the screen. In televisions the lamps are arranged in rows across the back of the panel. Figure 13 shows an exploded diagram of the LCD panel arrangement in monitors and televisions.
Figure 13 Location of CCFLs in LCD panels (monitor and television)

Figure 14 shows the number of lamps contained in different monitor and television screen sizes. It shows that LCD televisions contain a significantly higher number of lamps compared to monitors.

Figure 14 Number of CCFLs contained in LCDs by screen size and type

The manner in which the panels are disassembled mirrors the assembly route. To determine what recyclers may expect when processing LCDs, a number of other researchers have considered the breakdown of panels.

C. Environmental hazards of CCFLs

It is widely acknowledged that mercury is a danger to human health and the environment as it has bio-accumulative properties. Humans can absorb mercury in its many forms. The respiratory and gastrointestinal tracts are considered the main receptors, although the skin can also be at risk. The nervous system is the organ most vulnerable to mercury poisoning, with a fatal dose of mercury for humans considered to be approximately 100mg organic mercury. Smaller doses can result in symptoms such as tremors, weakness, and slowed mental response.

The rise of anthropogenic mercury in the environment has been a concern addressed by the EU in its 2005 mercury strategy. The EU strategy is one of reduction and control, with the phase out and substitution of mercury in industrial processes and products, where environmentally safer alternatives are available.
The policy of reducing mercury in the environment was applied to electrical and electronic equipment (EEE) placed on the EU market after August 2005 by the RoHS Directive. The Directive reduces the amounts of mercury allowed in EEE to 0.1% for homogeneous materials. However, exemptions within the Directive allow the use of mercury in the backlights of LCD equipment.

The main sources of mercury exposure to humans are those involved with occupational activities, such as product processing or mercury-bearing waste collection, storage and treatment. To provide protection for workers involved with mercury, regulatory occupational exposure limits to airborne mercury vapour in the workplace are in force.

The indicative occupational exposure limit values for mercury vapour have been set at 20μg/m⁢³ in the EU for an 8 hour time weighted average. While the mercury content of CCFLs stated by manufacturers is under 5mg per tube, the average large screen television can contain up to 20 or more lamps. Combined with the projected global LCD sales of 171 million units in 2010, the number of lamps requiring removal and mercury recovery in the future waste stream will be significant.

One study concluded that the mercury release from broken CFL lamps in confined conditions could pose an environmental health risk. This supported work into mercury vapour release and occupational exposure from handling and on-site crushing of fluorescent tubes in various scenarios. Concern over mercury escape from broken fluorescent lamps is not restricted just to mercury vapour, but also includes mercury compounds binding with other components in the tube.

An investigation was performed by the European Electronics Recycling Association into mercury vapour release from LCD equipment purposefully damaged during handling. The results showed a peak rise in airborne mercury vapour levels followed by a fall over a number of hours. Other studies have shown that the rate of evaporation of mercury from broken tubes is temperature dependent; elevated ambient temperature increases the levels of mercury vapour. This has ramifications for the whole chain of collection, storage, handling and treatment of LCDs in the waste stream.

**D. Methods of CCFL removal**

To date, there are no known automated recycling processes able to treat the broad range of LCD monitors and televisions containing mercury. Most research has concentrated on recovery techniques of valuable materials from LCD such as the liquid crystals, indium and glass.

The removal of CCFLs in a systematic approach has been considered using semi-automated processes compared with manual disassembly. The study concluded that manual disassembly was the preferred option. Other research has concluded that manual removal of CCFL in “an improved ventilation cabinet” was required.

The lack of available research means that information concerning effective ways to remove CCFLs is limited. A characterisation study of notebook displays has described a “shredding [device] with an appropriate mercury extraction unit” as the way to manage large volumes of LCD containing mercury.

However, others have recognised that if LCD displays are to undergo shredding, as is the case with the components of CRT equipment, then there is the risk of mercury emissions to air. Researchers acknowledge that shredding is not a viable option while the environmental effects of shredding mercury-containing LCDs is not known.

Research into a large scale recycling plant detailed the advantages of manually removing components containing mercury to avoid contamination of the output fractions. However, the same authors acknowledge that when considering hazardous substances, little is known about the relative efficiencies of hand sorting over a mechanical recycling process. Sharp Electronics of Japan together with Kansai Recycling Systems Co., Ltd. have jointly built a flat panel TV recycling line to deal with waste LCD, although the methods of CCFL removal are unknown.

An added complication is that there are many variations in LCD screen panel construction, from single screw lamp release through to full screen disassembly. Increasing difficulty in disassembly and lamp removal inevitably leads to more lamp breakages and mercury release. The difficulty in removal increases with larger screen size televisions due to the arrays of backlights mounted in the rear tray. Access to the backlights requires full panel disassembly, with manufacturers using a variety of fixing and retention methods. Moulding elastomeric rubber supports are extensively used to cover the wire to the tube electrode connection. Plastic clips mounted on the tray support the lengths of tubes. In most cases the tube retaining clips are designed for tube insertion and not removal. Figure 15 shows a typical arrangement and fixing methods of CCFL in the rear tray of an LCD television panel.
The delicate nature of these backlights, and the difficulty of removal and handling, means that breakages are common during disassembly.

A common theme considered by researchers into the recycling of LCD panels is that the removal of mercury is a key requisite in the treatment of this waste.

The WEEE Directive, and its proposed recast, emphasise that the collection and recovery of mercury from fluorescent tubes is to be treated as a priority for EU member states. For recycling facilities the removal and recovery of mercury from this waste stream, whether by manual or automated processes, will require demonstrable monitoring methods and auditable trails to ensure environmental protection.

**E. Mercury distribution in fluorescent lamps**

Research has shown that mercury exists within used fluorescent lamps in both elemental and compound forms. This research showed that the “mercury species Hg\(^0\), Hg\(^{+1}\) and Hg\(^{+2}\) occur in spent lamps, with the predominance of Hg\(^0\) and Hg\(^{+1}\) over the divalent species”. Others note that the operation of the lamps causes mercury to become chemically bound to various lamp components, as identified using a range of spectroscopy techniques. It was found that mercury interacted with the sodium in the glass and the barium which had accumulated around the lamp ends.

It has also been found that in used lamps the mercury is absorbed by the phosphor coating. The mercury species in the phosphor coating has been determined as Hg\(^0\), Hg\(^{+1}\) and Hg\(^{+2}\). Mercury concentrations of the phosphorus powder were considerably higher in spent lamps than in new lamps. In conventional CCFL operation, elemental mercury will be attracted to the caesium compound coated on the electrode. As this will affect the amount of material contaminated by mercury, these facts can have important implications when considering a strategy to effectively remove mercury from CCFLs. This is further compounded when considering how additional dispersal will occur if LCD devices are to be processed with CCFLs intact.

**F. Mercury removal from CCFLs**

Several methods have been identified for the removal of mercury from used fluorescent lamps, including photocatalytic techniques and physiochemical treatment. Both methods end up with a stable compound containing mercury. Concerns over potential mercury leaching means that storage in sealed containers or further treatment is needed. To avoid waste residues from chemical processes, the alternative is the use of thermal desorption techniques. Most research concerning the removal of mercury from CCFLs has tended to focus on this.

Although there are slight variations, the thermal desorption systems in general comprise:

- a crushing device;
- a pre-heated oven; and
- a condensing tank.
Research has identified a large temperature range over which mercury-bearing waste from fluorescent lamps is reduced to its elemental form. It concluded that part of this temperature range could be attributed to the mercury interactions with sodium in the glass.

A series of experiments have assessed thermal desorption techniques over different time periods (8-15 hours), and at different temperatures (350°C to 525°C). They concluded that the optimum conditions for mercury removal from CCFLs were a desorption time of 8 hours at a pre-heated temperature of 525°C, to achieve a 90% efficiency. Others introduced a reducing agent, sodium borohydride. This modified the desorption process to 300°C for two hours, achieving a 93% efficiency. Mercury is completely reduced when subject to a temperature range from 700°C to 850°C. More recent work suggests that temperatures can be lowered further if components can be removed from CCFLs prior to treatment.
Appendix II – Methods of Sample Preparation

The distribution of mercury and its compounds in CCFLs means that any crushing process will have to ensure that:

- mercury vapour escape is minimised during crushing;
- lamp materials including glass, electrodes and fluorescent powder are contained during crushing; and
- crushed lamps are retained in sealed containers to minimise mercury loss.

A. Sample Preparation Method 1
To prevent mercury loss during sample preparation, a stainless steel hammer mill with containment was used. This is shown in Figure 16. The hammer action was controlled by a pulse width modulated oscillator and could be varied to create different lengths of glass shard and fragmentation.

The lamp was fed into the mill through an aperture 0.5mm larger in diameter. A screw neck glass test tube was used to collect the lamp fragments. This tube was screw attached under the mill, sealing on a polytetrafluoroethylene PTFE ‘O’ ring seal.

Figure 16 Diagram of the CCFL hammer mill

To minimise the potential loss of mercury vapour during the crushing process, the CCFL lamps and glass tube collectors were cooled to 3°C. The crushed sample sealed in the collector tube was kept in a 3°C environment awaiting thermal desorption. The quartz desorption boats were also stored in the low temperature environment. This minimised mercury volatility when transferring the sample from the tube collectors to the desorption boats.

B. Sample Preparation Method 2
Lamp tubes were scored around their diameter with a tungsten carbide pointed glass cutter. The tube was scored at points A and B, as shown in Figure 17 below. Point A was adjacent to the glass seal of
the tube around the electrode wire. Point B was 10mm from the entry point of the wire into the glass tube.

![Image](image1.png)

**Figure 17** Section points A and B of a CCFL glass tube

The distance point B in all the case study lamps included the discoloured phosphors adjacent to the electrode. The discoloured phosphors are indicated by the arrow in Figure 18.

![Image](image2.png)

**Figure 18** Section of electrode assembly showing discoloured phosphor

The sectioning process caused breakage of the tube section to reveal deposits on the inside of the glass, adjacent to the electrodes shown in Figure 18. The length of tube remaining after partition of sections located at A and B at either end of the lamp were further sectioned into 100mm lengths. The tube lengths were supported in a retort stand and a stainless steel rod was used to remove the powder from the tube. The powder was collected in pre-weighed Petri dishes and subsequently weighed to determine the powder weight per length of tube. A similar procedure was performed to collect the discoloured powder from the 10mm section of tube removed between A and B. The small quantities available were stored in 0.2ml sealed vials.
C. Sample Preparation Method 3
The CCFLs were scribed around their diameter using a manual glass cutter, in proximity to the electrode contained in the lamp. The CCFLs were then broken to release the elemental mercury reservoir into a dry beaker. The electrodes were separated and stored separately in marked containers. The glass was removed and stored in a container for the glass fragments. The crushed tube and fluorescent powder were placed in a sieve container and then in an ultrasonic bath. The process separated the fluorescent powder from the glass shards. The powder and glass shards were stored in separate labelled containers.
Appendix III – Further detail on CCFL tests

A. HCl washing
No further detail.

B. Pyrolysis with CVAAS
A Lumex RA915 cold vapour atomic absorption spectrometer (CVAAS) was used. It is designed to measure mercury concentrations in air, complex materials and liquids. The pyrolysis technique involved the introduction of a small sample of the analysis material into a furnace operating at 550°C. Any sample containing mercury or compounds was thermally desorbed and the mercury vapour drawn through a detection cell. The cell was fitted with quartz windows allowing ultraviolet radiation to pass generated by a mercury vapour lamp.

The analysis software was calibrated using known sample standards (STD) and the absorption of mercury vapour from an analysis sample was calculated based on the standards calibration graph. The potential high concentrations of mercury from the samples required the use of a short path length detection cell to prevent saturation of the detector signal and contamination of the system from high levels of mercury vapour.

A high concentration 1000ppm mercury in Nitric Acid STD from Spectrosol was used to produce a calibration graph. To prevent mercury loss prior to the introduction of the standard solution into the pyrolysis attachment, measured aliquots were dispensed into the quartz sample holders containing crushed activated charcoal. The quartz sample holders and charcoal were pre-weighted and tared. The weight increase of the holder provided a known weight of standard. The introduction of the standard into the furnace vaporised the mercury, which was drawn through the detection cell. The pumping rate drawing the sample through the cell was 0.6 litres per minute. The mercury vapour concentration was analysed by the CVAAS. A calibration graph was created for the differing samples of standard solution.

**Fluorescent powder analysis**
Figure 19 shows the calibration graphs of the 1000ppm STD analysis with Figure 21 showing the analysis report. These calibration graphs and results were used to quantify the mercury content of the fluorescent powder samples from the sample lamp.

![Calibration graph](image19.png)

**Figure 19** Calibration graph for CCFL powder analysis
The calibration graph enables the analysis software to calculate mercury concentrations of the sample. Figure 20 shows the mercury detection curves showing sharp rise in detected mercury vapour as the sample is thermally desorbed of mercury. The detection curves are numbered to correspond to the sample number shown in the concentration report (Figure 21).

![Mercury detection curves of CCFL fluorescent powder](image)

Figure 20 Mercury detection curves of CCFL fluorescent powder

The average sample weight introduced into the furnace was 15mg of material. Integration of the area inside the detection curve of the samples is related to the standard analysis to allow sample mercury concentrations to be calculated. The report shown in Figure 21 shows the concentration levels measured in parts per million (ppm). The first items marked standard are the calibration for the analysis equipment. Sample 1-10 are the analysis results of the lamp powder from the sample lamps. Two control samples were tested for mercury content. These were (a) fluorescent powder from a lamp not exposed to mercury, and (b) a sample of fluorescent powder from a sample lamp previously tested by TGA analysis. Both the control samples showed no significant mercury content.
### Figure 21

Mercury concentration of standard and powder from CCFL in ppm

The mean concentration of the lamp powder is 2328 ppm.

### C. XRD

No further detail.

### D. SEM analysis of electrodes with EDS

To further investigate questions raised by observations drawn from initial analysis, a wider range of used lamps for SEM analysis was procured. The details of these lamps and their sources are shown in Figure 22 below.
The location and character of mercury in waste LCD backlights

<table>
<thead>
<tr>
<th>Source</th>
<th>LCD Panel Maker</th>
<th>Date</th>
<th>Number of lamps</th>
<th>Length mm</th>
<th>Diameter mm</th>
<th>Electrode material</th>
<th>Reference number</th>
</tr>
</thead>
<tbody>
<tr>
<td>15” Monitor</td>
<td>Chungwa</td>
<td>2002</td>
<td>2</td>
<td>310</td>
<td>2.2</td>
<td>Nickel</td>
<td>116</td>
</tr>
<tr>
<td>17” Monitor</td>
<td>AU Opto</td>
<td>2003</td>
<td>4</td>
<td>330</td>
<td>2.2</td>
<td>Nickel</td>
<td>85</td>
</tr>
<tr>
<td>26” Television</td>
<td>Chi-Mei</td>
<td>2007</td>
<td>12</td>
<td>590</td>
<td>3</td>
<td>Molybdenum</td>
<td>238</td>
</tr>
<tr>
<td>32” Television</td>
<td>Samsung</td>
<td>2007</td>
<td>16</td>
<td>720</td>
<td>3</td>
<td>Nickel</td>
<td>244</td>
</tr>
</tbody>
</table>

Figure 22 LCD equipment details of lamps for analysis

Initial analysis had raised the question of whether the mercury droplets attached to the electrode had been distributed during the breaking of the lamps. To reduce the mobility of the mercury droplets, the ends of the lamps were immersed in liquid nitrogen for five minutes to freeze the mercury prior to sectioning. The lamps were sectioned by the method described in Appendix II. The electrodes were withdrawn following sectioning at point A and placed on the carbon adhesive pads of the SEM aluminium mounts. The electrodes were retained as pairs for comparative observation and EDS analysis inside the SEM.

E. TGA analysis of electrodes with MVI

The TGA equipment used was a Shimadzu TGA-50 Thermal Gravimetric Analyser supported with TA-501 Thermal analyser. The thermal desorption pans were aluminium construction and designed for nominal sample weights between 20 and 40mg. The desorption atmosphere in the TGA was nitrogen gas flow, set at the manufacturer’s recommended flow rate of 50ml per minute. The temperature rise of the desorption chamber was set at 10°C rise per minute to achieved a final temperature of 550°C. A holding temperature of 550°C was set for 10 minutes after the final temperature had been achieved.

The weight of the sample was monitored during the experiments correlated to time and temperature. The analysis software produced graphs of weight loss versus time during the experiment. The experiments included testing control samples to verify equipment operation.

Control sample testing

Two grams of fine silica sand were introduced into a muffle furnace and the temperature raised to 550°C for a period of five hours to remove any traces of water and volatile compounds. The sample was cooled and sealed in Pyrex vial with a Teflon sealed screw top. The TGA was prepared for operation and a 20mg sample was introduced into the desorption pan. The sample was thermally treated over a 60-minute period. Figure 23 shows the weight change of the sample over the period.

---

3 The temperature of liquid nitrogen is 77K sufficient to lower the lamp end temperature to below the freezing point of mercury at 234K
The location and character of mercury in waste LCD backlights

Figure 23 Weight change of silica sand versus temperature

The 20mg sample weight of the silica sand showed a weight gain change of 0.072 mg over the period indicating there was no desorption of components from within the sample.

Electrode testing

The recommended weight for sample analysis in the TGA was 20-40mg. It also had to fit into the desorption pan. The overall length of a typical electrode with the glass seal assembly was 10mm and too large to fit within the pan. It was necessary to section the electrode removing the wire end and glass seal. The electrode end was placed in the desorption pan as shown in Figure 24.

Figure 24 Electrode sample preparation to fit TGA desorption pan
A screening study on a sample electrode was performed. The operating parameters for the TGA equipment are shown in Figure 25.

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Shimadzu TGA-50 Thermogravimetric Analyser fitted with TA-50 Thermal Analyser</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max temperature setting</td>
<td>550°C</td>
</tr>
<tr>
<td>Temperature rise</td>
<td>10°C per minute with 10 minute hold at maximum temperature</td>
</tr>
<tr>
<td>Gas flow</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>Gas flow rate</td>
<td>50ml per minute</td>
</tr>
<tr>
<td>Desorption pan</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Sample</td>
<td>Nickel Electrode from spent CCFL</td>
</tr>
<tr>
<td>Sample weight</td>
<td>21.90mg</td>
</tr>
</tbody>
</table>

**Figure 25** TGA operating parameters for nickel electrode screening study

The sample electrode was removed using the sectioning process described in Appendix II. The sample weight versus temperature rise is shown in Figure 26. In contrast to the thermal desorption of the fluorescent powder, the nickel electrode exhibited a significant weight loss in the temperature range from 70 to 198°C.

**Figure 26** TGA of sample CCFL nickel electrode

It was clear that material was being desorbed from the electrode, but without analysis of the exhaust gas from the TGA, the existence of mercury vapour was not confirmed. If the loss of material was due to the vaporisation of mercury, then the concentration of mercury within the exhaust gas would be detectable. Assuming that all the 0.389mg was mercury that was vaporised into a total flow volume of 50ml/minute multiplied by the loss period of 13 minutes, then the concentration of mercury vapour would be a theoretical 598 mg/m³.
These large concentrations would have proved difficult to measure without contaminating any measuring equipment with mercury. In order to determine the presence of mercury vapour, the exhaust gas from the TGA needed to be expanded into a larger volume of air. The diluted exhaust gas could then be sampled using CVAAS techniques to determine the presence of mercury during TGA.

A Shawcity Mercury Vapour Indicator (MVI) was used to sample the exhaust gas during the TGA of electrode pairs from CCFLs. The experimental setup of the TGA equipment and the MVI is shown in Figure 27. The MVI is a constant monitoring mercury vapour indicator with LCD readout capable of detecting mercury concentrations up to 2000 μg/m$^3$. The unit was fitted with a 0 – 2.5-volt analogue output suitable for data logging. The voltage output of the MVI was connected to a Picolog 1200 data logger. The exhaust gas was monitored during TGA operation for the four samples.

The MVI was calibrated to work in the nitrogen atmosphere of the TGA. An offset reading of 2μg/m$^3$ was set on the MVI as a baseline reading display. A TGA analysis of the control sample was monitored for mercury release and temperature rise of the exhaust gas. The results of this analysis are shown in Figure 28. The nominal increase in temperature in the expansion exhaust gas chamber was 14°C over the TGA period of 60 minutes. The MVI mercury monitoring was set at 2μg reading as baseline. The MVI showed no appreciable mercury measurements from the control sample. The experimental setup was further used for monitoring samples of electrodes from CCFLs.

![Figure 27 TGA mercury vapour monitoring schematic](image-url)

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Figure 28 Control sample TGA exhaust gas mercury vapour monitoring and temperature rise over analysis period
References


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