

Full Research Paper

Study on the leaching of mercury from compact fluorescent lamps using stripping voltammetry

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A study had been done on the determination of the amount of mercury present in an average CFL and the amount of mercury leached from the CFLs into the soil from where they are dumped. The extraction of the mercury from CFLs and the polluted soil was done by acid digestion. The electrochemical analytical method called Anodic stripping voltammetry (ASV) which is based on the potential dependent current measurement was used for the determination of mercury in the CFLs and the polluted soil. The determinations were done by standard addition technique in the exploratory mode. The results showed that the CFL contains 0.1175 mg/g of mercury. The soil from the spent CFLs dumped site reported a mercury concentration of 0.0149 mg/g. The leaching of mercury from the spent CFLs to the soil is confirmed by the analysis of soil from an artificially spiked spent CFLs dumped system.

Key words: Mercury, compact fluorescent lamp (CFL), anodic stripping voltammetry, leaching.

INTRODUCTION

Mercury's zero oxidation state Hg^0 exists as vapor or as liquid metal, its mercurous state, Hg^+ exists as inorganic salts, and mercuric state, Hg^{2+} may form either inorganic salts or organomercury compounds; the three groups vary in effects. It is used in thermometers, flu vaccines, dental fillings, fluorescent bulbs all of which end up in our oceans, lakes, streams and landfills, in fact, mercury ends up polluting our water supply (Srivastava, 2009). It is released into the air by the combustion of coal for electricity and may be transported from the air to soil and water by rain. The sources of mercury in urban storm water and sediment are improperly discarded compact fluorescent lights, electrical switches, thermometers, other mercury-containing devices and historical and ongoing industrial activities. Toxic effects of mercury include damage to the brain, kidney and lungs (Clifton, 2007). Mercury poisoning (also known as hydrargyria or mercurialism) is a disease caused by exposure to mercury or its compounds. Mercury poisoning causes personality changes, nervousness, and other mental

problems (Srivastava, 2009) and can result in several diseases, including acrodynia (pink disease), Hunter-Russell syndrome, and Minamata disease (Davidson et al., 2004). Nowadays all forms of mercury are recognized to be a cause of a variety of adverse health effects, including neurological, renal, respiratory, immune, dermatologic, reproductive and developmental sequelae (Risher and Amler, 2005; Rooney, 2007). Mercury in the air eventually settles into water or onto land where it can be washed into water. Once deposited, certain microorganisms can change it into methylmercury, a highly toxic form that builds up in fish, shellfish and animals that eat fish. Birds and mammals that eat fish are more exposed to methylmercury than any other animals in water ecosystems (U.S Environmental Protection Agency, 2010). For foetuses, infants and children, the primary health effect of methylmercury is impaired neurological development. Methylmercury exposure in the womb can adversely affect a baby's growing brain and nervous system which leads to impaired cognitive thinking, memory, attention, language and fine motor and visual spatial skills. Effects of methylmercury exposure on wildlife can include mortality, reduced fertility, slower growth and development and abnormal behavior that

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affect survival, depending on the level of exposure (U.S Environmental Protection Agency, 2010). The Prevention of Food Adulteration Act and Rules, 1955 has declared Hg as a poisonous metal (Subarna et al., 2008). Maximum contaminant level of inorganic mercury in drinking water set by Environment Protection Agency and Food and Drug Administration is 0.002 ppm. The Bureau of Indian Standards has laid down its safety limits in drinking water at 0.001 mg/L.

Compact fluorescent lamp or fluorescent tube is a gas discharge lamp that uses electricity to excite mercury vapor. It contains a very small amount of mercury sealed within the glass tubing – an average of 4 mg (Frequently Asked Questions, Information on Compact Fluorescent Light Bulbs (CFLs) and Mercury, 2008). Fluorescent lamps rely on mercury as the source of ultraviolet radiation for the production of visible light (Jang et al., 2004). The excited mercury atoms produce short-wave ultraviolet light that then causes phosphor to fluoresce, producing visible light. A fluorescent lamp converts electrical power into useful light more efficiently than an incandescent lamp.

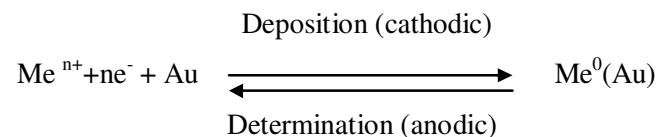
The release of mercury to the environment during these products' life cycles has contributed to widespread mercury pollution. Broken CFLs, if they behave similarly to broken fluorescent tubes, can be expected to release perhaps as much as 40% of the mercury they contain in a two-week period, at the end of which period they would very likely be entombed in a landfill (Aucott, 2008). If a fluorescent lamp is broken, a very small amount of mercury can contaminate the surrounding environment. About 99% of the mercury is typically contained in the phosphor, especially on lamps that are near their end of life (Floyd, 2002).

Mercury in CFLs is present as elemental (or metallic) mercury. Mercury exposure may occur through the air, as elemental mercury vaporizes readily (essentially becomes a gas) and can thus be inhaled into the lungs. Exposure of mercury on lungs by breathing elemental mercury is generally more dangerous than getting it absorbed through skin. Once inhaled, the mercury vapor can damage the central nervous system, kidneys and liver (Golb, 2007).

The conventional methods for measuring total mercury include absorption spectrometry (dithizone colorimetry), neutron activation analysis, and cold vapor atomic absorption spectrometry (Logar et al., 2001). Piezoelectric sensor technology and electrochemical technology were reported to be used for mercury determination (French et al., 1998). An overview of different analytical methods using ICP/MS as a detector to determine mercury species in environmental samples had been reported by Hintelmann (2000).

The unusually high sensitivity and the selectivity of stripping voltammetry is based on the fact that the determination is done in two steps. First step include the accumulation of the substance (usually metal) on a

polarisable micro electrode surface at a suitable constant potential called deposition potential which continues up to a controlled deposition time. Second, the metal deposits from the electrode are dissolved in the solution called the stripping step during which the potential is scanned with a certain rate and the current generated is measured during stripping step. The removal of the accumulated analyte species from the working electrode, the real determination step is based on oxidation processes in case of anodic stripping voltammetry:



The determination by this technique is more sensitive by a factor of 10^3 to 10^5 so that the detection limits are between 10^{-9} to 10^{-11} mol/L. Resistance of the solution is reduced by adding background electrolyte. As the accumulation and the determinations take place at the same electrode without needing to change vessel, the systematic errors by contamination or evaporation are kept at a very low level.

MATERIALS AND METHODS

Study area

In order to study the leaching of mercury to the soil, samples were collected from Manjoody in Calicut district of Kerala, India, a CFL disposal and solid waste dumping site.

Chemicals

Chemicals and Reagents: Hg^{2+} stock solution was commercial mercury standard solution in $c(\text{HNO}_3) = 2$ mol/L containing 1000 mg/L Hg(II) (Merck), mercury working standards were prepared daily from the stock solution containing 1 mg/L Hg(II) in $\text{HNO}_3 = 0.01$ mol/L and it was volumetrically standardized. The electrolyte called primary solution used in the cell contained 0.2 mol/L perchloric acid (18.8 ml of 70% HClO_4 in 1 L), 3 mmol/L of sodium chloride (0.34 g in 1 L) and 1 mmol/L sodium salt of EDTA (1.5 g Na_2HEDTA in 1 L).

Ultrapure water (Millipore MilliQ Plus 185 system) was used for the preparation of all solutions, which were deoxygenated with nitrogen. All the glassware was stored in acid solution in closed containers in order to avoid contamination.

Instrumentation

The mercury measurements were performed in differential pulse mode in 797 VA Computrace (Metrohm, Schweiz-Suisse-Switzerland) with the use of 797 VA Computrace 1.2 control software. 797 VA Computrace systems for voltammetric analysis use the working electrode Au-RDE, 3 mm diameter (2000 rpm), glassy carbon as auxiliary electrode and $\text{Ag}/\text{AgCl}/\text{KCl}$ (3 mol/L in water) as the reference electrode, with $\text{Ag}/\text{AgCl}/\text{KCl}$ (3 mol/L in water) as the internal system and primary solution as the external

system. Mercury determination was done by using solid state electrode Rotating Gold Electrode (Au-RDE) with anodic stripping voltammetry (ASV). The study was aimed at the determination of the mercury content in CFLs and leaching of the mercury to the soil from the CFLs disposal sites. Anodic stripping voltammetry (ASV), an electrochemical analytical method, based on the potential the dependent current measurement in electrochemical cell was used for determination of mercury in CFLs and the polluted soil. Metrohm 797 VA Computrace in differential pulse mode was used for the determination. ASV is the most efficient electrochemical technique for the trace analysis and had been widely used for detection of heavy metals in various samples because of its remarkably low (nanogram per liter) detection limits (Logar et al., 2001).

Experimental

The determination of mercury in CFL was done using anodic stripping voltammetric measurements in differential pulse (DP) mode with standard addition technique in the exploratory mode.

Initial setup of the analyser

The ASV parameters for the pretreatment of the cell were: Purge time 300 s; deposition potential 300 mV, deposition time 90 s; equilibration time 10 s; cleaning potential 1300 mV, pulse amplitude, 50 mV; start potential, +370 mV; end potential, +730 mV; voltage step 1.984 mV; voltage step time, 0.1 s; sweep rate 19.8 mV/s; and peak potential for Hg 640 mV. The rotation speed of RDE was of 2000 rpm. The electrode was electrochemically cleaned *in situ* by applying a potential of 1100 mV for 30 s which was high enough to ensure Hg²⁺ desorption, as it was checked with reproducible blank experiments with Hg²⁺ solutions. After carrying out the electrode cleaning procedure, the deposition potential of +370 mV was applied for 120 s (at which the Hg was accumulated) followed by 10 s of equilibrium period and cathodic potential scan between +370 and +730 mV.

Measurements

The measurements were performed as follows: 10 ml of ultra pure water and 10 ml primary solution were added to the polarographic vessel and purged with nitrogen for 5 min, and the blank voltammogram was registered in order to nullify the presence of any contamination. In the next step of the determination method, 0.1 ml digested sample was added to the vessel. The voltammogram for the analyte was registered. Afterwards, 0.1 ml of 1 ppm Hg²⁺ standard is added to the vessel as the first addition of the standard. Corresponding voltammograms were recorded to ensure the reproducibility. Then, 0.1 ml of 1 ppm Hg²⁺ standard was again added to the vessel as the second addition of the standard. After every addition, the solution in the cell was purged with nitrogen for 1 min and the differential pulse voltammetric curves for each addition was registered.

Determination of the quantity of mercury in CFL

The CFL taken for the study was 15 W, 850 Lm, 240 V and 50/60 Hz. The glass material where the mercury was coated was crushed and made into fine powder in a mortar under laboratory conditions. From the crushed CFL glass material, 3 g was weighed and the extraction of the mercury was done with nitric acid and perchloric acid and heated for 2 h. Then it was filtered and was made up to 100 ml. Then the extract was analysed for mercury using voltammetric analyser.

Determination of mercury in the soil

In order to study the leaching of mercury to the soil near or under the CFL dumping site, one soil sample was collected from Manjoody in Calicut, a CFL disposal and solid waste dumping site. The soil was taken at a depth of 10 cm in the CFL dumped land. 1 g of the collected soil was air dried and crushed into fine powder. The metal extraction was done by acid digestion using nitric acid and perchloric acid. The extract was made up to 100 ml and analyzed for any residual mercury, from abandoned CFL's, leached into the soil without getting vaporized into the atmosphere using voltammetric analyser.

Verification of leaching of the mercury from the CFL

In order to confirm the leaching of mercury from CFLs, twenty CFLs were crushed under laboratory conditions and put in half square meter area of land. The system was kept undisturbed for 10 days. Then the soil was analyzed for any residual mercury using voltammetric analyser. The soil was also tested for mercury before dumping the CFLs.

The result obtained from the software output denotes the actual concentration of mercury in the soil. In voltammograms, the area of the peak is the power that is the voltage × current.

The voltammetric analyser was further standardized using 1 mg/L mercury solution (prepared from 1000 mg/L stock solution, from Merck) as sample and was analysed for mercury concentration. The results were found to be accurate with low correction factors.

RESULTS AND DISCUSSION

The present study focused on the leaching of mercury from abandoned broken CFL's in the CFL disposal site. The proposed voltammetric method was found ideal to determine the residual mercury amount that leached into the soil from broken abandoned CFL's without getting vaporized into the atmosphere. In Au-RDE, Hg²⁺ is readily adsorbed on the Au electrode surface (French et al., 1998). The determination of mercury was done for CFL sample, soil from CFL dumped area. Figure 1 shows the voltammogram of the analysis of mercury in CFL material. The voltammogram provides qualitative and quantitative information of the analysis. The analysis of the CFL glass material extract in 100 ml using the voltammetric analyser showed mercury concentration of 3.524 mg/L which corresponds to a concentration of 0.1175 mg/g of CFL glass material.

The voltammogram in Figure 2 shows the analysis of mercury in soil collected from the CFL waste dumped site. The analysis of the soil extract in 100 mL using the voltammetric analysis showed mercury concentration of 0.149 mg/L which corresponds to a concentration of 0.0149 mg/g of soil in the CFL dump site.

The analysis of mercury in soil in which, the CFLs were to be artificially spiked, for the confirmation of the leaching of mercury from the CFLs (considered as the blank soil measurement) was also performed. The analysis of the soil extract in 100 ml using the voltammetric analyser showed zero mercury concentration. The analysis for mercury in the soil artificially spiked

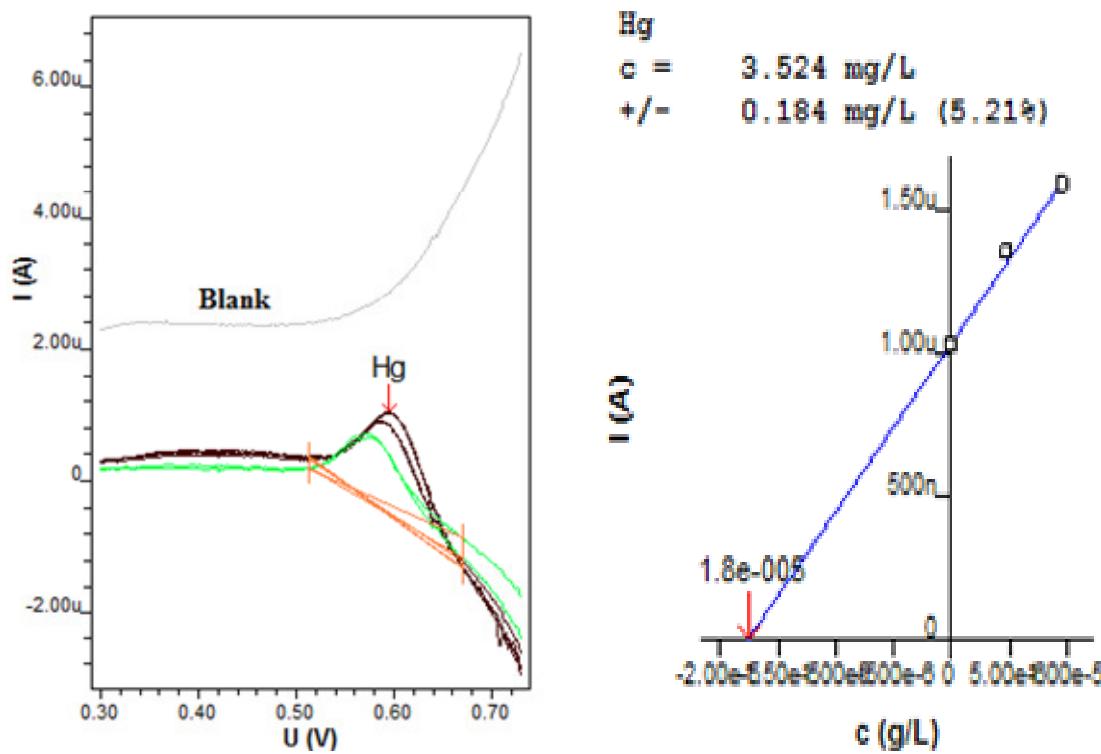


Figure 1. Differential pulse voltammograms obtained during the determination of Hg^{2+} in CFL lamp with standard addition method (1.0 ppm Hg^{2+} standard) in NaCl - EDTA primary solution. Deposition potential 0.64 (± 0.1)V during 90 s; scan rate 19.8 mV/s; equilibration time 10 s. 100 ml extract from 3 g CFL glass material.

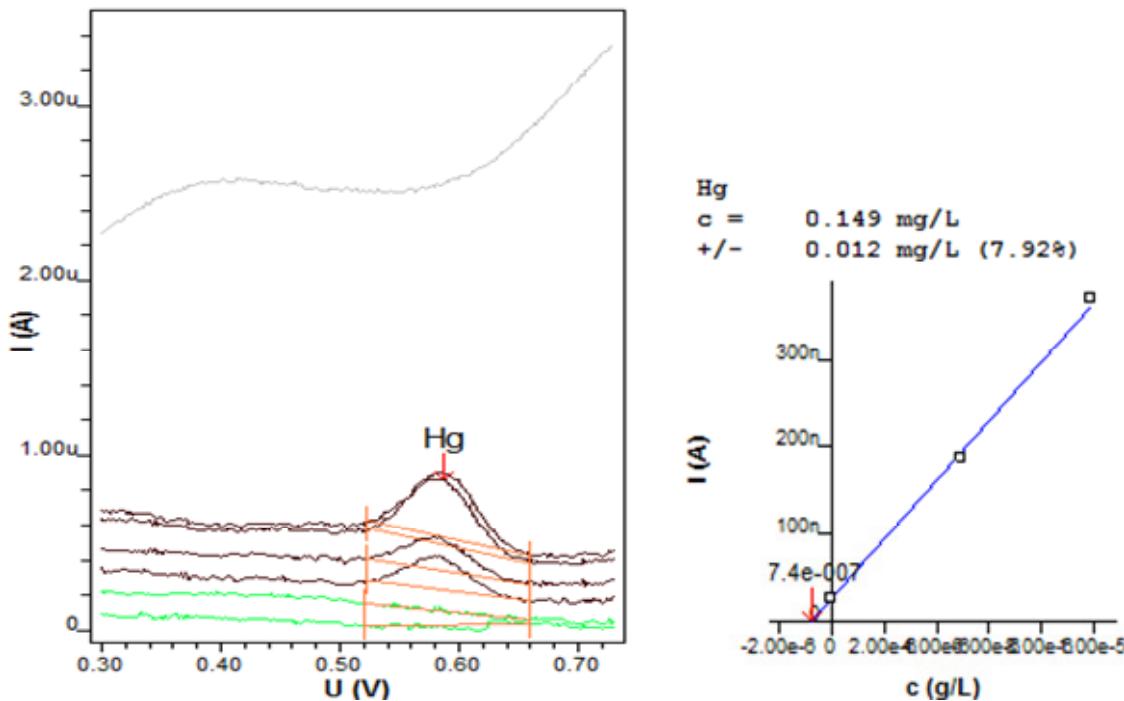


Figure 2. Differential pulse voltammograms obtained during the determination of Hg^{2+} in soil under the CFL waste dump site with standard addition method (1.0 ppm Hg^{2+} standard) in NaCl - EDTA primary solution. Deposition potential 0.64 (± 0.1)V during 90 s; scan rate 19.8 mV/s; equilibration time 10 s. 100 ml soil extract from 1 g.

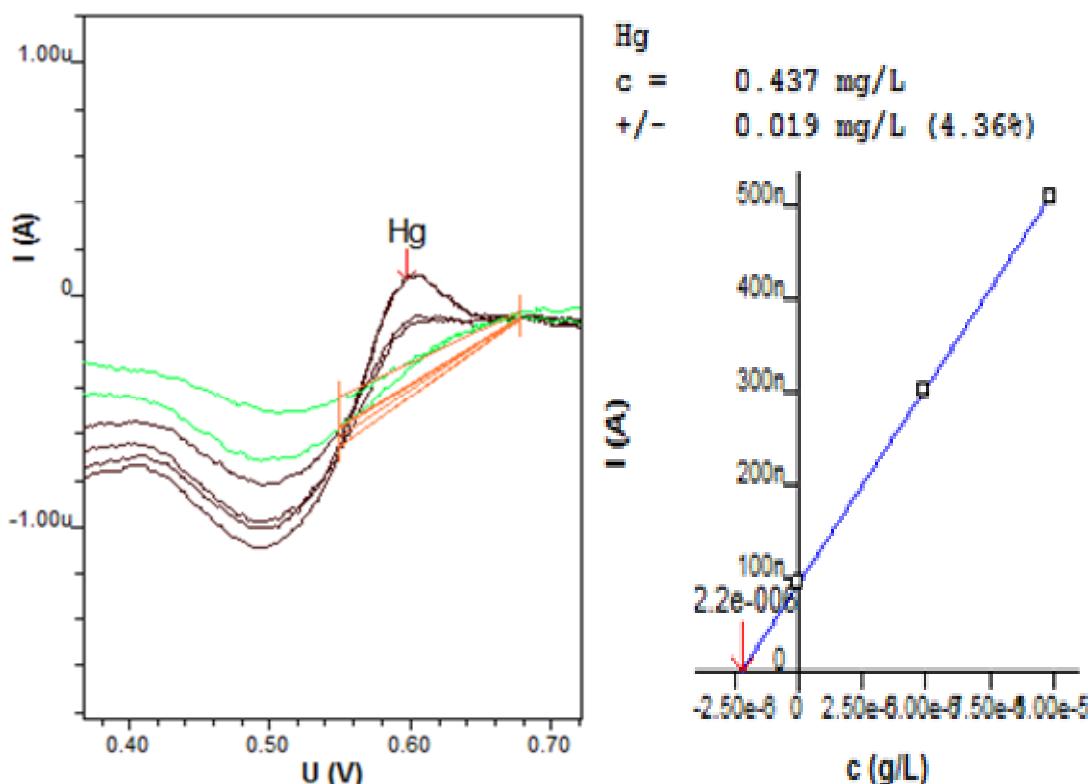


Figure 3. Differential pulse voltammograms obtained during the determination of Hg^{2+} in CFL waste dumped soil after 10 days with standard addition method (1.0 ppm Hg^{2+} standard) in NaCl-EDTA primary solution. Deposition potential 0.64 (\pm 0.1)V during 90 s; scan rate 19.8 mV/s; equilibration time 10 s. 100 ml soil extract from 3 g soil is diluted to 100 ml. The results are given in the Table 1.

Table 1. The concentration of mercury in various samples.

S/ No.	Sample	Conc. of mercury, mg/g
1	Spent CFL powdered	0.1175
2	Soil from control site (no CFLs)	0.0100
3	Soil from Manjoodi from CFL waste dumping site	0.1490
4	Soil from artificially spiked site with CFL s	1.456

with CFLs, after ten days showed a concentration of 1.456 mg/g of soil. The results reported a significant increase in the concentration of mercury in the soil. This confirms the leaching of mercury into the soil. The voltammograms for this analysis is shown in Figure 3 and Table 1.

Conclusion

The study indicated that an average CFL contains a mercury concentration of 0.1175 mg/g. If the broken CFLs are not properly handled, the mercury present in the lamp can contaminate the soil in and around the waste dumping sites. An average of 0.15 mg/g of mercury was

detected in the site. This may finally get convert to methyl mercury and may reach in nearby water bodies through water runoff. Adequate precaution should be taken before disposing the CFL along with other solid wastes.

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