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Short communication

A straightforward wet-chemistry method for the determination of solid and gaseous mercury fractions in Backlight Cold Cathode Fluorescence Lamps

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ABSTRACT

Backlight Cold Cathode Fluorescence Lamps (B-CCFLs) are already applied in many electronic consumer products such as LCD screens, flat screen TVs, and laptop monitors. In consequence, an increase of such products entering the waste streams can be expected in the near future. As a result of the mercury (Hg) employed in such lamps, the development of recycling techniques to create a best practical environmental option for appropriate end-of-life strategies are necessary. For this purpose the knowledge about speciation in terms of solid and gaseous state of Hg in such lamps is inevitable. However, analytical techniques to discriminate solid and gaseous Hg require a special setup, not available in most routine laboratories. Thus a straightforward and cost efficient analytical technique is of need.

In this work we describe sample preparation procedures and analysis techniques, which only require equipment already available in most routine laboratories. The volatile fraction is extracted with a $KMnO_4$ solution utilizing a novel approach, taking the advantage that the B-CCFL glass tubes have a negative pressure. Thus the extraction solution is directly sucked into the tube where the volatile Hg-fraction is immediately extracted. Subsequently, the solid fraction is dissolved via microwave assisted pressure acid digestion after cryo-milling. Analysis for both fractions took place employing a cold vapor atomic absorption system.

To prove the new method is fit for purpose, spiking experiments and analysis of reference materials (when available) was performed with recoveries being between 90% and 110%. First results obtained for a stack of lamps from an used LCD-TV display reveal that solid Hg fractions in all lamps show a variation of 20% between samples whereas the gaseous Hg content can vary up to 600%.

1. Introduction

Backlight Cold Cathode Fluorescence Lamps (B-CCFLs) are already applied in many electronic consumer products for the luminescence of flat screen TVs, liquid crystal displays (LCDs), and laptop monitors [1,2] and occasionally in certain automotive applications like instrument panels and navigation systems [3]. A B-CCFL consists of an evacuated glass tube (diameters of about 0.5–0.1 cm) filled with mercury (Hg) and two cathodes on each end (usually a wire or plate inside each end of the glass tube that an electrical current can be applied to). Inside the tube is coated with a phosphorous layer, which transfers photons emitted from Hg into a bright white light.

In the European Union vehicles and electronic equipment containing B-CCFLs fall under the scope of the Directive on end-of-life vehicles (ELV) [4] and the Directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS) [5], respectively. Both directives prohibit in principle the use of mercury. Exemptions for applications may be granted if the state of the technique is such that substitution of mercury is not possible. In Switzerland the restrictions laid down in the ELV and RoHS directives are implemented in the Ordinance on Chemical Risk Reduction (ChemRVV) [6]. According to the ELV directive, mercury containing B-CCFLs are only permitted in vehicle types approved before 1st July 2012 and in spare parts for these vehicles. In contrast the RoHS directive sets currently no limitation on the use of mercury in B-CCFLs. However, from 1st of January 2012 the content of mercury in B-CCFLs was restricted to an amount of 3.5 mg–13 mg depending on their lengths.

According to a United Nations University report [7] the amount of mercury from B-CCFLs of LCD screens sold in Europe was estimated to be 2.8 t for the year 2006. Considering this number and the fact that B-CCFLs are more and more replaced by

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LED backlights, the amount of mercury from B-CCFLs entering the waste stream is expected to be increasing in the near future [8] and achieving a maximum in the year 2014 [1]. Within the EU Waste Electrical and Electronic Equipment (WEEE) directive [9] B-CCFLs are classified as hazardous and have to be recovered by specialist recycling. However, a recent publication [10] discussing the problems of mercury recycling from B-CCFLs, stressed that the processes to remove and recycle these lamps are not well developed. It was stated that there is a lack of data characterizing the components containing mercury, making the development of recycling techniques to create a best practical environmental option difficult.

In consequence, appropriate analytical methods are of need to set measures for end-of-life waste management. Still, appropriate analysis of Hg in B-CCFLs for end-of-life strategies is not an easy task because the aggregation state of Hg found in cold cathode lamps can change after use. During production, the lamps are first filled with metallic Hg and afterwards evacuated. Due to the low boiling point of mercury and the decreased pressure, new lamps contain mostly volatile Hg. During use, the volatile Hg reacts with the phosphorous layer and the glass wall and is transferred into solid Hg species. This process, called “mercury starvation”, is nonreversible and thus goes along with a loss in efficiency. In consequence, depending on the time of application B-CCFLs contain different levels of volatile and solid Hg.

Until now, most attempts for the determination of Hg in fluorescent lamps utilize different extraction or leaching techniques. Following atomic absorption or emission spectroscopy only the total mercury concentration in the samples could be determined [11,12]. Beside total mercury determination, speciation of Hg in the phosphorous layer and the soda-lime glass by application of a thermodesorption apparatus coupled to atomic absorption spectrometry was reported to estimate Hg release e.g. during thermal waste treatment [13]. It was reported that most of the mercury is bound in the phosphorous layer of the CCFL and to a lesser extent to the glass and the cathodes. However, for appropriate measures in end-of-life treatment, not only the knowledge of the total or solid Hg constituents but also the volatile fraction is of importance. In consequence, proper sample preparation is necessary to reliably obtain volatile and solid Hg concentrations for B-CCFLs. Until now, the only technique described for this purpose is the cold spotting method [14]. However, this technique requires a modified analytical instrument setup. This setup includes a special cooling cell to solidify the volatile Hg in the B-CCFL, which is not available in most of the routine labs. In consequence, a more straightforward method for the quantification of the total, solid, and gaseous Hg fractions in B-CCFLs is of need.

2. Experimental

2.1. Chemicals

Nitric acid (HNO_3, 65% w/w, p.a.), Sufuric acid (H_2SO_4, 96% w/w), Hydrochloric acid (HCl, 32% w/w, suprapur), Hydroxylammonium chloride ($HONH_2 \cdot HCl$, p.a.), Sodium Chloride (NaCl, p.a.), Tin chloride ($SnCl_2 \cdot 2H_2O$, p.a.), mercury(II) chloride ($HgCl_2$, p.a.), mercury(II) oxide (HgO, p.a.), and potassium permanganate ($KMnO_4$, p.a.,) have been purchased by Merck (Germany). A Millipore Milli-Q A10 has been employed for the production of 18 MΩ cm de-ionized (DI) water.

2.2. Extraction of volatile Hg

The volatile Hg fraction in B-CCFLs was extracted with a 2% (w/w) aqueous $KMnO_4$ solution. Fig. 1 depicts how the extraction procedure was performed in detail. The B-CCFL glass tube was dipped with one end into a glass beaker containing 50 mL of the $KMnO_4$ solution. Afterwards, the lower end of the tube was opened carefully with a compressor. As a result of the vacuum in the glass tube, the $KMnO_4$ solution was immediately sucked into the glass tube and complete wetting was achieved to extract the volatile Hg. After the extraction solution was allowed to sit for 2 min (longer times did not show an improvment in extraction efficiency), the B-CCFL tube was rinsed with DI water twice and the extract was acidified with 1 mL of 96% (w/w) H_2SO_4. In consequence, extracted volatile Hg is oxidized and stabilized according to:

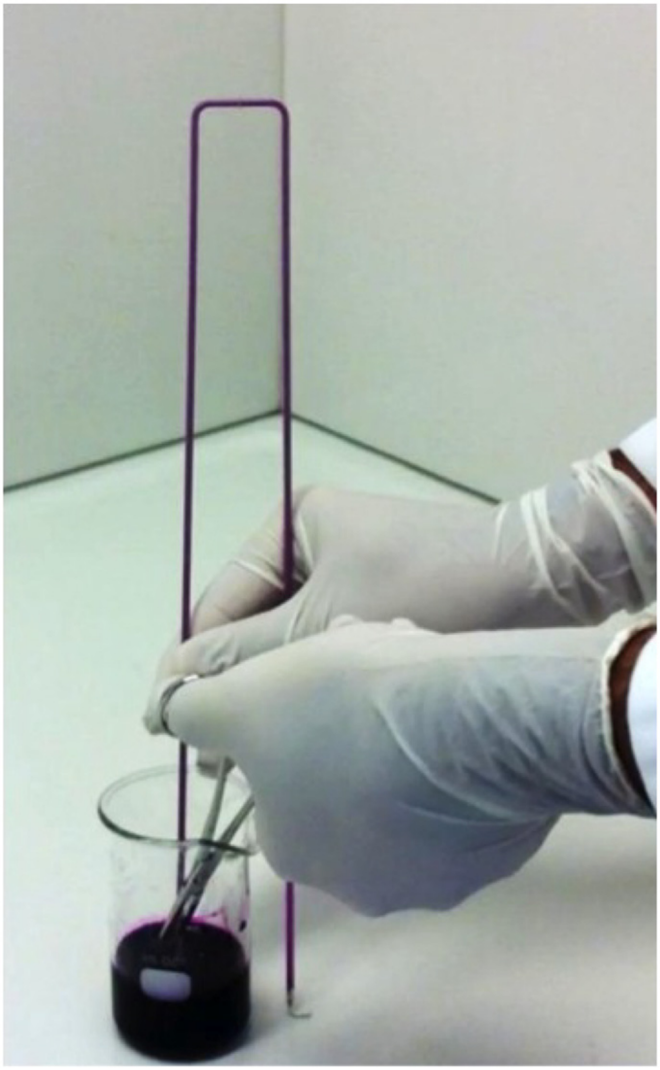

Fig. 1. Extraction procedure of volatile Hg in B-CCFLs.

$$5Hg^0 + 2KMnO_4 + 16H^+ \rightarrow 5Hg^{2+} + 2Mn^{2+} + 8H_2O + 2K^+ \quad (1)$$

Afterwards, the extract was filtered and transferred to a 200 mL volumetric flask. Before analysis 10 mL of a 6% (w/w) HONH2 . HCl / 6% (w/w) NaCl solution for pre-reduction of Hg^{2+} to Hg^+ was added and the flask was filled to the mark with DI-water.

2.3. Extraction of solid Hg

A Retsch “Cryo-Mill” (12 mm stainless steel milling balls) with liquid nitrogen as coolant was employed for sample homogenization of the B-CCFL glass tubes (and residues from filtration of the $KMnO_4$ solution). Subsequent extraction of the volatile Hg fraction, the B-CCFL glass tubing including the cathodes was transferred into the mill. After a 3 min pre-cooling period a 3 min milling procedure with a frequency of 25 Hz was performed. For extraction and mineralization of solid Hg from the milled glass powder, a microwave assisted pressure digestion system (MLS Start, Mikrowellen Labor System GmbH) was employed. For this purpose, 0.2 g of the cryo-milled B-CCFL glass tubes were mixed with 5 mL 65% (w/w) HNO_3 and the dispersion was heated in sealed teflon vessels (ramp to 195 in 20 min, 20 min at 195 °C). After digestion the HNO_3 extract was decanted from the milled glass particles and filled to 100 mL with DI water. Immediately an aliquot of 10 mL was transferred to 15 mL polyethylene vessels and stabilized by addition of 10 μL 2% (w/w) $KMnO_4$.

2.4. *Cold vapor atomic absorption spectroscopy*

A Perkin-Elmer FIMS 400 cold vapor atomic absorption spectrometer (CV-AAS) was employed for the quantitative analysis of volatile and solid Hg after $KMnO_4$ or microwave extraction. A 1% (w/w) HCl and 1.1% (w/w) $SnCl_2$ solution was used for the reduction of Hg. Argon as a carrier gas with a flow of 70 mL/min was employed to transport the cold vapor into the measurement cell. The concentration of Hg was determined by external calibration using a 1000 mg/L Hg standard diluted with DI water and stabilized with $KMnO_4$. Determination of the detection limit (LOD) was performed according to DIN 32645 with the indirect method.

3. Results

3.1. *Extraction of volatile Hg from CCFLs*

For the determination of the volatile Hg fraction from B-CCFLs appropriate sample preparation techniques have to be performed. Conventional sample preparation by only crushing and milling of the glass tubes is permitted to prevent loss of the volatile fraction. Cold spotting, like already stated in the introduction, require a special extraction cell, which is not available in most routine laboratories. Thus we decided to strike another path attempting specific extraction with a solution of $KMnO_4$ in excess, well known to be able to absorb volatile Hg quantitatively [15] e.g from coal power plant gas streams [16]. Although levels of Hg in such streams are lower than in the case of B-CCFLs, the proposed method is a static extraction procedure with an excess of MnO_4^- to mercury ratio. Theoretically (see Eq. (1)) the employed extraction solution is able to oxidize several grams of elemental mercury and thus quantitative extraction can be expected for levels in the μg range found for B-CCFLs. Furthermore, due to the fact that the glass tube is evacuated, the negative pressure is high enough to sop up an extraction liquid and completely fill the glass tube when opening (see Fig. 1). In consequence, the extraction of the volatile Hg can be done directly in the B-CCFL tube itself by careful opening of the tube with a compressor directly in the extraction solution.

Anyhow, with such a procedure it is possible that also soluble Hg species or powder from the wall layer can be co-extracted, falsifying the results. According to personal communication with producers of B-CCFLs the layer coating is sintered and not in the form of a powder and the solid Hg-amalgam is limited in solubility and thus not extractable with aqueous solutions. To guarantee that only the volatile fraction is completely extracted from the sample, tests with a set (10 tubes) of used B-CCFLs from a LCD PC monitor were performed. One part (5 tubes from the array) of the B-CCFLs were extracted directly after opening and the remaining 5 tubes were extracted by leaching after the tubes were opened in the fume hood and the volatile Hg were led to escape into the atmosphere overnight. In Fig. 2 the results for the directly determined and evaporated samples are presented. For samples leaching directly after opening a concentration of 1100 ± 400 μg of volatile Hg per sample was determined. For the set of samples where the Hg was evaporated overnight an almost 300 fold lower concentration (3.7 ± 0.8 μg) volatile Hg was determined. The results prove, that only an insignificant amount of Hg from the phosphorous layer is extracted with the herein proposed method and thus the method can be used to specifically determine the volatile Hg fraction in B-CCFLs.

As a result that no reference material for gaseous mercury is currently available, appropriate method validation is challenging. Spiking of the samples with known amounts of volatile Hg would be a possibility; however not easy to perform as well as a risk because of the known toxicological facts when mercury is inhaled. Thus, to determine the reliability of the extraction, a spiking

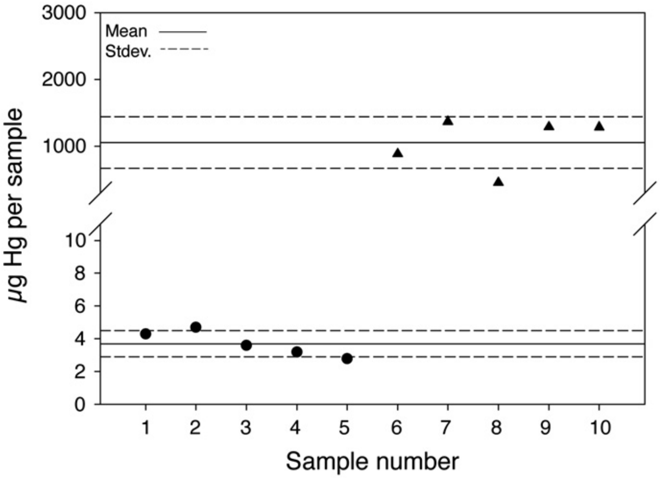

Fig. 2. Hg concentrations for samples leached after the volatile Hg being evaporated overnight (circles) and directly extracted with $KMnO_4$ after opening (triangles) with the herein proposed method (*LOD* = 0.7 μg Hg per sample).

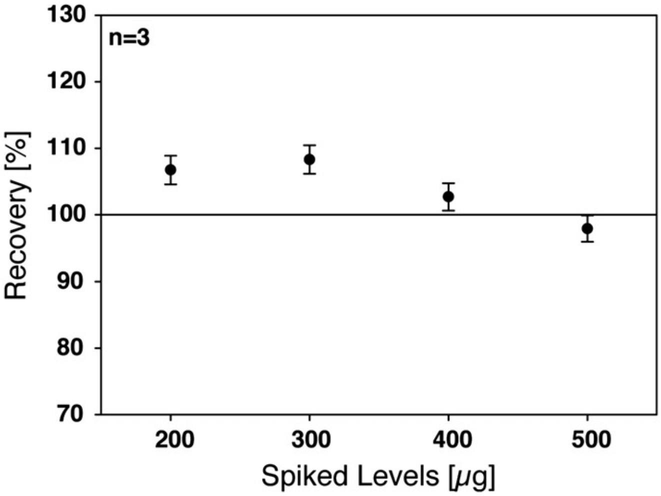

Fig. 3. Recovery of spiking experiment with solid mercury for an extract containing 420 μg mercury (*LOD* = 3.9 μg Hg per sample).

experiment with solid metal mercury was performed. In Fig. 3 the results for such an experiment are presented. For the original sample an amount of 420 μg per sample was determined. Spiking levels from 200 up to 500 μg Hg resulted in recoveries from 110% to 99%.

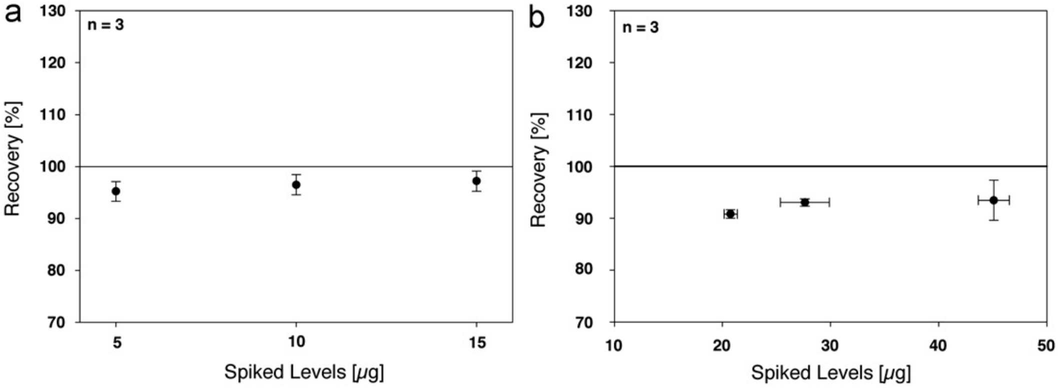

Fig. 4. Recoveries from spiking experiments for the solid Hg fractions in B-CCFLs conducted with (a) soluble Hg-species ($HgCl_2$) and (b) insoluble Hg-species (HgO; $n=3$, $LOD=0.4$ μg Hg).

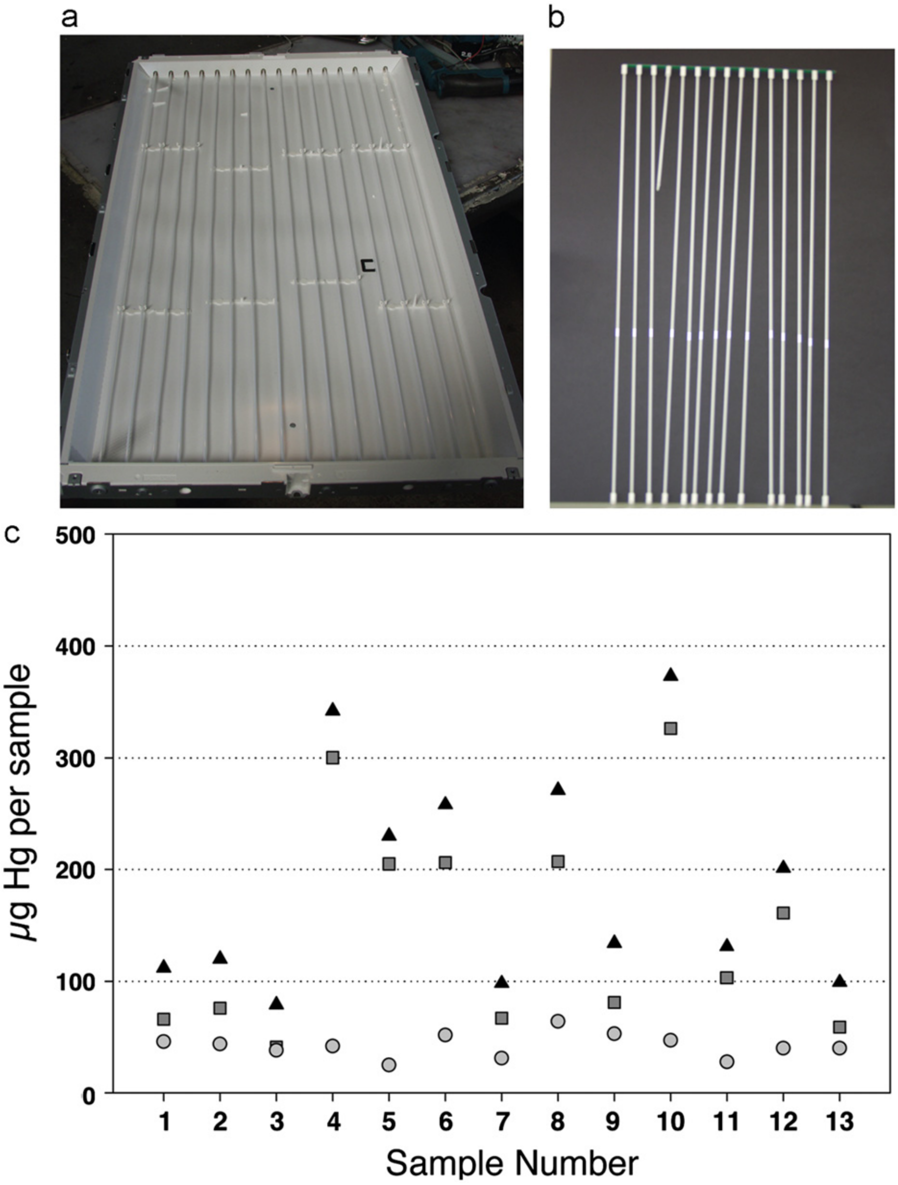

Fig. 5. (a) B-CCFLs mounted in a frame of a LCD-TV and (b) unmounted from the frame before extraction and analysis. (c) Solid (light gray circles), volatile (dark gray rectangles) and total Hg (black triangles, as sum of volatile and solid Hg fractions) in 13 intact B-CCFLs from the unmounted LCD-TV.

3.2. Extraction of the solid Hg fraction

For the extraction of the solid Hg fraction from B-CCFLs, which is mainly found as hardly soluble Hg species, a microwave assisted acid digestion step has to be performed. For this purpose the sample has to be homogenized beforehand digestion. To prevent possible loss of mercury, a ball mill cooled with liquid N_2 was employed. To ensure that this method is fit for purpose analysis of two reference materials with different levels of mercury as well as spiking experiments were performed. Because no reference materials with certified mercury levels specifically for the analyzed type of samples are available, recoveries of Hg levels from one soil (BAM U-110, 51.5 ± 4.1 μg/g Hg) and one marine sediment (NRC PACS-1, 4.57 ± 0.16 μg/g Hg) reference material were determined. For both reference material samples the determined value was in between an error of less than 10% from the certified levels (54.8 ± 0.4 μg/g and 4.71 ± 0.3 μg/g Hg for BAM U-110 and BRC PACS-1, respectively).

In Fig. 4(a) and (b) the results from the spiking experiments for solid Hg are presented. The employed B-CCFL was first extracted such as described in Section 3.1. For the spiking experiment, a soluble Hg (5, 10, and 15 μg Hg as a $HgCl_2$ solution in nitric acid) and insoluble Hg (15–50 μg Hg as solid HgO) species was added to the teflon vessels containing the milled B-CCFLs and HNO_3 before microwave digestion. For all levels a recovery of 95%–97% ($HgCl_2$) and 91%–96% (HgO) was obtained, indicating a slight loss of Hg during the microwave digestion procedure but still in a range lower than 10%.

3.3. First results for the analysis of used B-CCFLs.

For the analysis a stack of B-CCFLs from an used and damaged flat panel LCD TV brought in for recycling was analyzed. The TV was carefully dismantled (Fig. 5a and b) and 13 of the intact B-CCFLs were analyzed according to the proposed extraction methods. In Fig. 5(c) the determined values for volatile, solid, and total Hg (as a sum of both species) are presented.

All samples show a solid Hg concentration in the range of 50 μg (40 ± 10 μg). The transfer from volatile Hg to solid Hg is in a relation to the time of usage. As a result that all B-CCFLs in the screen have been used for the same time it is expected that also the solid Hg concentrations in all samples be in the same range. In contrast, the determined volatile Hg fraction concentrations vary between 50 and 320 μg (150 ± 100 μg).

The results imply that the amount of mercury in B-CCFLs is varying significantly (from 80 up to 380 with a mean of 190 ± 100 μg Hg for our investigated samples). This finding is also in agreement with numbers published by Singhvi et al. [11] for CCFLs energy saving light pulps, where a variation of almost 400% in between lamps from different producers as well as a standard deviation of 20%–57% when analyzing different lamps ($n=20$) of the same type was reported. The high RSD numbers are explained by the manufacturing process variability, which is according to our findings also valid for B-CCFLs used in flat screen TVs.

4. Discussion

The herein proposed analytical method for the determination of volatile and solid Hg fractions in B-CCFLs is a straightforward procedure, which can be easily implemented into the routine lab environment. No modification of instrumentation or special sampling equipment is necessary.

The first results obtained for used B-CCFLs from a flat screen TV demonstrate the necessity for a proper analysis of such samples. Because of the large variability of Hg-levels, the analysis of a whole stack rather than only one sample is necessary to set appropriate measures for end-of-life treatment as well as to test for compliance with given regulations for Hg concentrations in such products.

In the future the method will be used to obtain the volatile and solid Hg fraction in used and new B-CCFLs to build up a database. Furthermore, the application of the method will be tested for other types such as compact fluorescent lamps (energy saving lamps) and linear fluorescent lamps. Thus, more precise numbers are obtained for the amount of Hg introduced to the market from mercury containing lamps and the development of appropriate end-of-life recycle strategies can be supported.

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