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LEAD HAZARD EVALUATION FOR CATHODE RAY TUBE MONITORS IN BRAZIL

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Abstract – Cathode ray tube (CRT) monitors are electronic equipment mainly made of glass, polymers and metals. These devices became obsolete because of emerging technologies such as LCD, LED and plasma; thus generating a huge stockpile of e-waste worldwide. In this CRT study, a natural leaching simulation (NBR10005) was performed to determine the toxicity of this e-waste. The standard NBR 10005 procedure was performed for 7 different monitors. The results show all samples are hazardous according to local environmental law (NBR 10004) due to lead leaching. The CRT panel is lead free, while the CRT funnel and neck have about 20% of lead oxide in their composition. Moreover, six optimum thermal lead removal procedures were performed and the NBR 10005 procedure was repeated. The results reveal that vacuum atmosphere and the addition of 5% carbon graphite as reducing agent are optimum conditions to turn the CRT into a non-hazardous waste. Three out of six parameters were capable of satisfactorily removing the lead and turning the post-procedure waste lead-leaching safe.

Keywords: cathode ray tube, computer monitor, lead removal, recycling, WEEE

INTRODUCTION

WEEE

Electrical and Electronic Equipment (EEE) is – but is not limited to - equipment which is dependent on electric currents or electromagnetic fields in order to work properly. Waste of electric and electronic equipment (WEEE) includes not only the equipment itself, but also all the components, subassemblies and consumables which are part of the product at the time of discarding (European Union, 2002). WEEE contains a significant number of precious metals, many of which are being recovered through different studies: examples include the recovery of copper (Kasper et al., 2011), silver (Dias et al., 2016), gold (Bigum et al., 2012) and palladium (Duygana & Meylan, 2015). Improper WEEE handling and recycling may lead to health problems as these equipment contain harmful substances such as toxic metals and flame retardants (Lecler et al., 2015). In 2005, Brazil was ranked third in the world in the generation of e-waste from computers, only behind the USA and China (Gerbase & Oliveira, 2012). The 2008 estimate is that 710,000 tons of e-waste were generated in Brazil, meaning almost 20% of the Brazilian e-waste is waste from CRT monitors (Araújo et al., 2012). Despite having proper landfills for the disposal of CRT monitors, most of them end up in improper landfills or in no landfill at all (Oliveira, 2013)

Cathode ray tube monitors

The CRT used in television and computer screens represents one of the main sources of e-waste as flat screens have replaced them over the last ten years (Lecler et al., 2015). CRTs are made up of 85% glass and 15% plastics and metals. The glass has three components: funnel, panel and

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**Corresponding author*: Pablo Dias. E-mail: pablo.dias@ufrgs.br neck (Fig. 1). The chemical composition of these parts are similar among different producers, but are different among themselves (Méar, et al., 2006). The panel component is the heaviest part and it contains elements such as barium, strontium, and yttrium. The other two components usually contain lead in their composition; the total amount of lead in a CRT may reach 3 kg (Lecler et al., 2015).The lead content varies according to the manufacturer, but the average concentrations have been published in several works (Table 1). According to Menad (1999), the lead in the CRTs is responsible for the radiation shielding and for stabilizing the glass.

Recycling CRTs

As stated by Okada (2015), a material containing lead may scatter and result in oral intake of the dispersed lead by humans, which ultimately results in health problems. Lead is also toxic for other animal cells and plants (Menad, 1999).This statement encourages researches that aim to remove the lead from the waste CRT. Veit et al. (2015) studied various thermal parameters to extract the lead from the funnel glass; their optimum result removed 92% of the lead. Okada (2015) extracted lead from the glass of CRT by using hydrochloric acid and by melting the glass under different oxidizing conditions. Minfei et al. (2016) studied the detoxification and reutilization of CRT funnel glass by using a thermal reduction aided with acid leaching; which was able to remove up to 95% of the lead from the glass.

It is clear that recycling waste of CRT is important not only for mitigating environmental issues, but also for maximizing the value of the waste (Zhang et al., 2016).As reported in several international publications, waste of CRT monitors represents an environmental threat and yet it has not been classified under Brazilian law. This study ranks waste of CRT monitors according to Brazilian NBR 10004 (ABNT, 2004) norm and performs different detoxification methods to evaluate their efficiency in downgrading a hazardous waste to a non-hazardous waste.

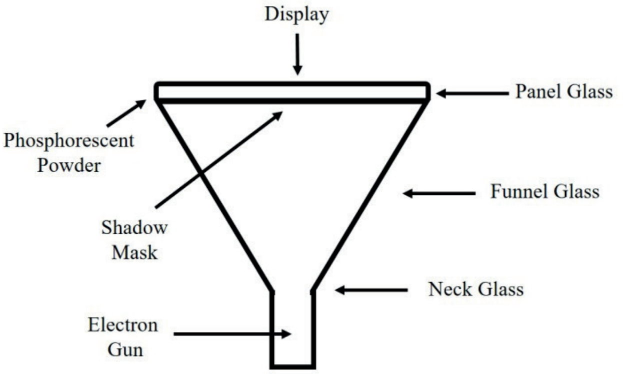

Figure 1. Illustration of a CRT highlighting the three different glass components on the right.

MATERIALS AND METHODS

Characterization

Cathode ray tube monitors were collected for these experiments; their manufacturing year varied from 1988 to 2005. The monitors were manually dismantled using tools such as pliers, screwdriver, electric saw, saw, hammer, vise. To ensure personal safety of the operators, the following personal protective equipment (PPE) were worn: lab coat, protection goggles, gloves and trousers. The monitors were weighed and their parts were separated and sorted into four categories: external frame, printed circuit boards (PCBs), cathode ray tube (CRT) and other components (wires, bobbins, bolts). In order to open the vacuum sealed tubes, the monitors were placed behind a wooden shield and the metallic threads were removed using a set of pliers. The parts dismantled from the CRT monitors are shown in Fig. 2.

The CRTs were split into three, according to the previous delimitation (Fig. 1). Neck, funnel and panel parts (Fig 3.) from several CRTs were separately milled in an A4R hammer mill (Tigre, São Paulo, Brazil), then in a ball mill (Groschopp, Iowa, USA). In order to make sure the monitor samples used in this work had similar lead distribution to the ones from previous studies (Table 1), the three milled glass parts were analyzed by X-ray fluorescence (XRF) using an Axios Advanced (PANalytical, Almelo, Netherlands). The obtained results encouraged a study regarding the hazard potential of CRT monitors.

Lead Hazard Evaluation

Seven CRTs monitors were submitted to the Brazilian standard leaching procedure to evaluate their hazard potential. The procedure followed the Brazilian norm NBR 10004 (ABNT, 2004), which determines the limit of lead that can be leached from any solid waste and NBR 10005 (ABNT, 2004), which determines the leaching procedure for the waste. The NBR 10004 displays a list of known

Table 1. Summary of lead content in waste CRT for different studies

Author	Lead Content		
	Panel (wt %)	Funnel (wt %)	Neck (wt %)
Menad (1999)	3	23	32
Musson et al. (2000)	0-3	24	30
Méar et al. (2006)	0-3	19-23	25
Chen et al. (2009)	Not reported	24	Not reported
Veit et al. (2015)	0.03	22	59
Mingfei et al. (2016)	Not reported	23	Not reported

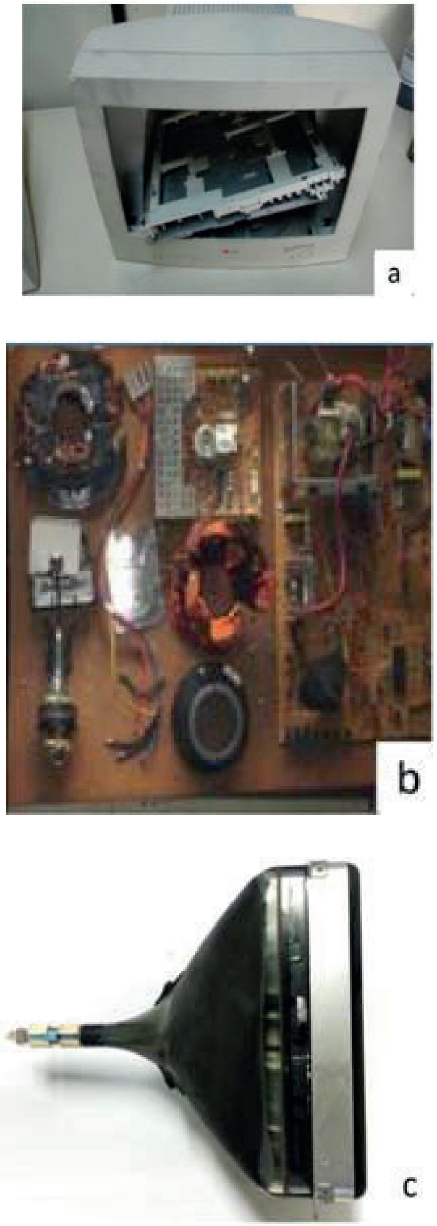

Figure 2. Dismantled parts from a CRT monitor. a) External Frame b) PCBs and other components c) CRT.

hazardous materials and their characteristics and can be related to the Code of Federal Regulations title 40, subtitle 260-265 of the United States (40 C.F.R. § 260-265). Wastes that are not characterized in the NBR 10004 should be classified according to their leaching potential, which is evaluated using the NBR 10005. The procedures presented the NBR 10005 simulate the leaching that may occur to a non-sheltered waste; a flowchart of the norm is presented in Fig. 4. The solutions obtained from the 7 monitor samples were analyzed by atomic absorption spectroscopy (AAS) using a FS240 equipment (Varian, California, USA).

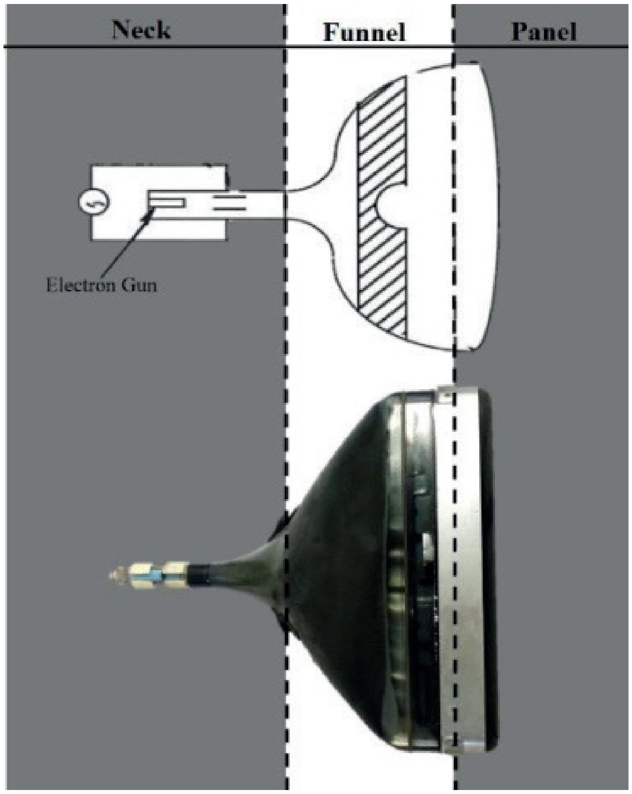

Figure 3. The division of the cathode ray tube. CRT illustration (above) and a photograph of an actual CRT used in our experiments (below).

Lead Removal and Evaluation

The next step in this study was the removal of lead from the CRT by thermal processes. The chosen glass component for this procedure was the funnel glass because it presented high lead concentration. A tube furnace structure was assembled to control the process (Fig. 5).

The funnel glasses from different CRT were all mixed together. A sample name (A, B, C, D, E and F) was assigned for each set of parameters used in the furnace procedure (Table 2). Samples A, B, D and F were put into the furnace with carbon graphite (99.9% grade) as a reducing agent. Samples C and E were placed in the furnace with no reducing agent. The gas flow for samples A and B was set at 10 L/min. The pressure inside the tube for samples E and F was set at 1.3 kPa. All samples weighed 20g (glass + reducing agent). The samples were placed inside alumina crucibles, which were then placed inside the furnace. The choice of the parameters used in the procedure was based on the work of Veit et al. (2015), that optimized the conditions for removing lead from CRT monitors (Table 2). The possible redox reactions are as follows (Veit, et al., 2015):

$$PbO_{(s)} + C_{(s)} \leftrightarrows CO_{(g)} + Pb_{(g)}$$

$$2PbO_{(s)} + C_{(s)} \leftrightarrows CO_{2(g)} + 2Pb_{(s)}$$

$$PbO_{(s)} + C_{(s)} + O_{2(g)} \leftrightarrows PbCO_{3(s)}$$

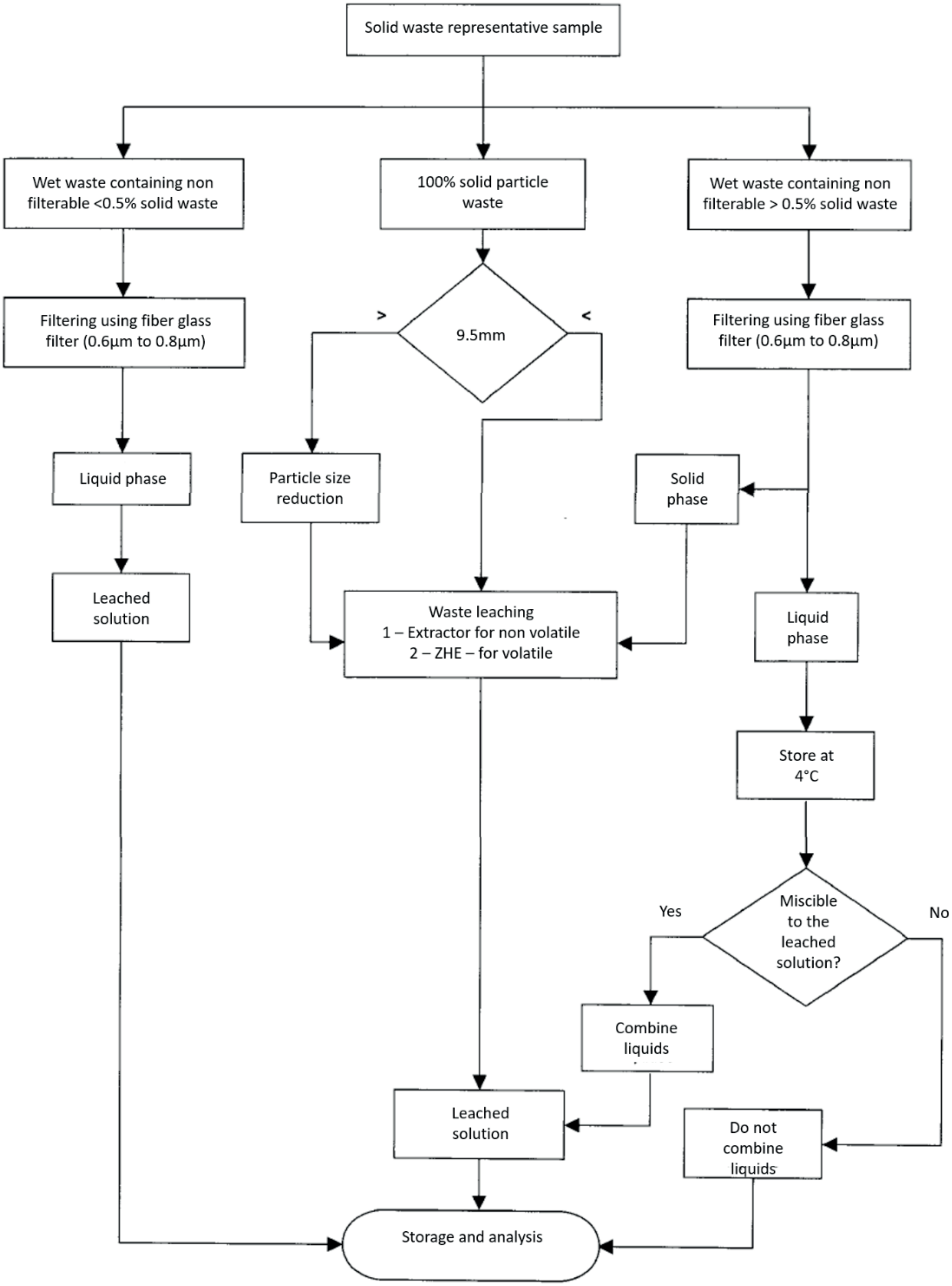

Figure 4. NBR 10005 - Flowchart of the procedures. Adapted from ABNT (2004).

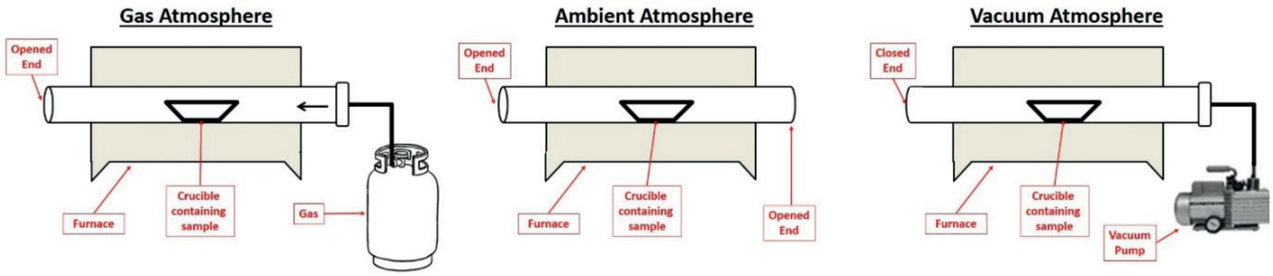

Figure 5. Schematic illustration of the furnace setup for different atmosphere conditions.

Table 2. Parameters used to remove lead from the CRT funnel glass (Veit et al., 2015).

Sample's Name	Temperature (ºC)	Atmosphere	Reducing Agent (wt %)	Reaction Time (h)
A	1200	Argon	5	6
B	1200	Carbon dioxide	5	6
C	1200	Ambient	0	14
D	1200	Ambient	5	24
E	800	Vacuum	0	24
F	800	Vacuum	5	18

The next step was intended to evaluate whether the lead removal had been able to convert the CRT from a hazardous waste to a non-hazardous waste according to the Brazilian regulation. Thus, the standard Brazilian NBR 10005 procedure was repeated with the samples that had been submitted to the thermal process (A, B, C, D, E and F). The solutions obtained from the procedures were analyzed by atomic absorption spectroscopy and the results were compared to the limits shown in NBR 10004.

RESULTS

Characterization

The weights obtained from the dismantling demonstrate that the glass represents the majority of the monitor's mass (Table 3). Fig. 6 shows the funnel glass after the milling procedure.

The XRF results from CRT parts confirmed that lead is present in the funnel and in the neck while the panel is lead free, as shown in Table 4. These XRF results show that the lead concentration reaches about 20% in the funnel glass and in the neck glass. It also shows that, apart from the concentration of lead, barium, zirconium and strontium (in panel), the three glass parts have similar composition. It should be noted that XRF determines the atoms present in the sample and not the compounds. However, given that the sample was glass, the XRF equipment assumes the atoms are in their most oxidized state – resulting in the chemical compounds shown in Table 4.

Table 3. Mass distribution of the dismantled components of the CRT monitor.

Component	Mass (kg)	Weight %
External frame	2.40	20.00
PCBs	0.95	8.00
CRT (glass)	7.10	59.00
Other components	1.55	13.00
Total	12.00	100.00

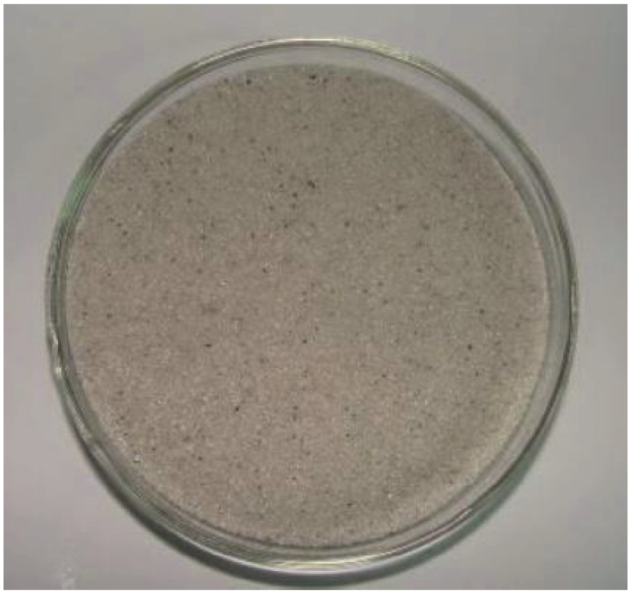

Figure 6. Milled funnel glass sample

Table 4. XRF results obtained from the glass extracted from the CRT monitors.

Oxide	Panel (wt %)	Funnel (wt %)	Neck (wt %)
SiO_2	66.5	59.3	56.2
PbO	0.03	19.6	22.1
K_2O	6.65	6.98	6.69
Na_2O	7.38	5.78	5.55
CaO	1.57	3.4	3.28
BaO	6.25	Not detected	0.17
SrO	6.79	0.06	0.08
Al_2O_3	1.79	1.77	1.79
Fe_2O_3	0.38	0.83	1.39
ZrO_2	1.49	0.03	0.02
Co_3O_4	0.01	0,01	0.02
TiO_2	0.42	0.03	0.15

Table 5. AAS results from the leached samples obtained from the NBR 10005 standard procedure.

Sample	Lead concentration (mg/L)		
	Neck	Funnel	Panel
1	9.5	347.3	Not detected
2	4.2	58.0	Not detected
3	25.2	81.2	Not detected
4	6.5	6.6	Not detected
5	14.9	9.2	Not detected
6	12.8	174.5	Not detected

Table 6. AAS results from the leached samples obtained from the NBR 10005 standard procedure after the lead removal procedure.

Sample	Lead concentration (mg/L)	Hazardous? (NBR 10004)
A	5.84	Yes
B	2.51	Yes
C	1.13	Yes
D	0.68	No
E	0.32	No
F	0.13	No

Lead Hazard Evaluation

The results regarding the hazardousness of the 7 CRTs leached according to the NBR 10005 procedures and analyzed by AAS are displayed in Table 5. The results show that all 7 samples are above the permitted standard (NBR 10004), 1 mg/L. This indicates that CRT monitors are a dangerous waste and that they should not be discarded in non-controlled landfills; particular attention is drawn to the values 347 mg/L and 174 mg/L (funnels from samples 1 and 7, respectively). The panel glass did not present any leached lead, which is logical, since no lead was found in the previous XRF (Table 4). The big variance among the samples is probably related to the year the monitors were manufactured. Before 1990, CRT did not use high voltage in the electron gun, and thus, did not need as much lead in the glass for shielding (Webster, 1999).

Lead Removal and Evaluation

The results from the AAS obtained from the samples that had undergone the thermal process are displayed in Table 6. Samples A, B and C are still above the permitted standard according to NBR 10004. Thus, the lead removal conditions were not effective to downgrade the hazardousness of the waste. On the other hand, samples D, E and F are below the standard. The next step was intended to evaluate whether the lead removal had been able to convert the CRT from a hazardous waste to a non-hazardous waste according to the Brazilian regulation. Thus, the standard Brazilian NBR 10005 procedure was repeated with the samples that had been submitted to the thermal process (A, B, C, D, E and F). The solutions obtained from the procedures were analyzed by atomic absorption spectroscopy and the results were compared to the limits shown in NBR 10004.

Thus, these three procedures detailed in Table 2 are effective in removing lead from the glass of the CRT to the point where it becomes a non-hazardous waste.Vacuum atmosphere is ideal for the removal of lead from CRT glass as samples E and F performed better than sample D. Vacuum, however, is not necessary when adding 5% reducing agent and allowing a 24 h reaction time in an ambient atmosphere (sample D). Sample F displayed the best results as it was able to reduce the lead in the glass to a minimum in comparison to the other 5 samples.

CONCLUSIONS

The key conclusions from this study are as follows:

- The standard Brazilian procedure (NBR 10005) showed that lead can be leached from the CRT monitors. The lead concentration in the leached solution demonstrates that CRT monitors are a hazardous waste to the environment and are classified as *Class I – Dangerous Waste* according to NBR 10004.
- The lead removal evaluation showed that parameters from samples D, E and F can remove the lead from CRT monitors to an environmentally safe level. Best results were observed in sample F that was processed with the following parameters: temperature of 800ºC, vacuum atmosphere, addition of 5% carbon graphite as reducing agent and reaction time of 18h.

Future studies should evaluate the hazardousness potential of other elements such as barium and strontium.

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