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RESEARCH ARTICLE

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DETERMINATION OF PB CONCENTRATION LEVEL IN CATHODE RAY TUBES BY ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

Objectives: In the present work were employed methods for the determination of lead glass from cathode ray tubes. For the analysis, they used small pieces of CRT components (television and computer) from different manufacturers and dismantled by hand. After milling, vitreous samples were analysed by SEM, EDS and XRD to determine the particle size and the elemental composition of the investigated material. For this study was used a mixture ratio of 1: 1: 1: 4 by weight (electron gun neck, funnel and screen). For the analyzes by GFAAS samples were digested in acid medium (HCl 2.4 ml, 1.2 ml HNO₃, 2.4 mL HF and 2.0 mL H₂O), where about 125mg of the glass sample. They were added PTFE bottle. The total concentration of lead in CRTs and GFAAS was determined by the values found for two mixtures from different samples were (735.52 ± 6.12) mg kg⁻¹ and (886.61 ± 5.49) mg kg⁻¹. The toxicity of the sample was evaluated using the standard NBR 10004: 2004 for solid waste. The mixture was subjected to leaching tests and the leaching extract was analysed by atomic absorption spectrometry flame (FAAS) and optical emission spectrometry with inductively coupled plasma (ICP OES). The results indicated that about 85% of Pb present in the leach residue. The leaching tests for CRTs waste reached the Class I values (hazardous waste) according to the ABNT NBR 10004: 2004, due to the high concentration of lead present in its composition.

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INTRODUCTION

The development in the electrical and electronic products sector, where there is an increase in the speed of technological innovation, in the diversity of products, in the massification of consumption and in the trend towards miniaturization has been contributing to an increase in the volume of solid waste. One of the main effects of this technological development is the specialized media, competitive prices and the ease of credit lines. The electronics industry strives to create the illusion of obsolescence and, they are one of the main effects of this

accelerated technological development, convincing people that it is necessary to change their computers, cell phones, cameras and other equipment, with more applications, reduced sizes and with more attractive models to conquer the consumer, in shorter and shorter periods [1]. The rapid advancement of technology and the low cost of acquisition annually lead to the replacement of millions of these types of devices, resulting in an increase in the generation of so-called electronic waste. The generation of this waste is related to the consumption habits of each culture. The lack of management policy or controlling inspections of the generation and destination of this, especially in developing countries, has aggravated the level of

environmental degradation with direct and indirect effects on public health, since they are not collected and treated properly [1]. Electronic waste contains hazardous substances and its disposal on the ground in sanitary landfills, as well as tires, batteries and fluorescent lamps are harmful to health and the environment [2]. Contamination of the environment occurs through the lack of waste management when they are disposed of improperly, causing serious problems to the environment by contaminating the soil, water, plants and animals and, consequently, the food chain [3]. Due to these negative effects, the European Community appointed a Commission with the purpose of gathering the necessary information to subsidize the formulation of a policy for the proper management of this waste. In 2000, the Commission presented to the European Parliament a preliminary document with justifications based on several important studies related to the risks of WEEE and which served as a basis for the formulation and discussion of two Directives aimed at the proper management of this waste [4]. In 2002, member states and the European Parliament approved Directive 2002/96/EC, which establishes rules governing the proper management of this waste, and Directive 2002/95/EC, on the restriction of the use of certain hazardous substances in electrical equipment and electronics. They entered into force on February 13, 2003, when they were published in the Official Journal of the European Community According to these Directives, which establish rules governing the proper management of this waste and restrict the use of certain hazardous substances in electrical and electronic equipment, the levels of Cr, Hg, Pb and Cd in WEEE must be less than 0.1%, 0, 1%, 0.1% and 0.01%, respectively, of the mass of the homogeneous material [4-6]. According to a report by the United Nations Environment Program (UNEP), currently 40 million tons of electronic waste are generated per year in the world, coming from developed countries. The European Union alone generates between 8.3 and 9.1 million tons annually [7]. The management of this waste is a significant problem for industrialized countries, there has been a considerable increase in this waste due to the replacement of computer monitors and televisions that have cathode ray tubes (CRT) by liquid crystal screens (LCD), causing a serious environmental problem when discarded improperly, as they contain compounds such as lead, cadmium, strontium, barium, arsenic and antimony in their composition [8]. The National Solid Waste Policy (law 12305) approved in 2010 provides for the proper disposal of electronic waste. Among the various types of waste are cathode ray tubes (CRT) used in monitors [9]. Due to this problem, advances in national legislation are needed, contributing to the management of waste electrical and electronic equipment (WEEE), in this work, a study was carried out to determine the concentration of Pb in CRT waste and comparing it with according to Toxicity Characteristic Leaching Procedure (TCLP) (SW-846 Method 1311; USEPA 2003) and Associação Brasileira de Normas Técnicas 10004.

Experimental CRT samples: CRT glass residues were obtained from the dismantling of disused monitors in the laboratory of the Department of Physics and Chemistry at Universidade Estadual Paulista "Julio Mesquita Filho". 99/242 V, 60 Hz frequency and computer monitor model QN15VSPPN/XAZ, 100/240 V network, 60/50 Hz frequency. The CRTs were broken into closed containers to avoid environmental contamination. Then, samples were collected from different parts of the CRT: electron gun, neck, funnel and screen. The values of the average sizes of the microparticles and the SEM images of the components of the investigated CRTs with a magnification of 5000x are presented in Table 1. In preliminary results, it was observed that the particles have varied sizes smaller than 9 μm , according to the ABNT NBR 10005:2004 is the size required for the procedure for obtaining the leached extract.

Table 1. Mean sizes of microparticles in SEM images

CRT Components	Average sizes of microparticles (μm)	
	PC	TV
a) Electron gun	7.07	880
b) Neck	10.61	7.31
c) Funnel	8.65	8.99
d) Screen	10.10	8.78

Reagents and Solutions: The solutions for obtaining the leached extract were prepared from analytical grade reagents and deionized water (ultra pure water resistivity 18.3 M Ω cm) obtained by the Mega Purity system and the standard solutions were prepared using deionized water and purified in a purifier system of water-GEHAKA with conductivity (0.35 $\mu\text{S}/\text{cm}$). The glassware and polyethylene materials used were washed with soap and water, then with deionized water, and then immersed in a 10% HNO₃ bath for 24 h. Subsequently, these materials were washed with deionized water (Millipor). The reagents used were H₂O₂ (Merck, Darmstadt, Germany), H₂SO₄ (Merck Darmstadt, Germany), HNO₃ (Merck, Darmstadt, Germany), the latter being double-distilled. Chemical modifier solution (1000 mg L⁻¹ Pd) was prepared from 10000 mg L⁻¹ Pd (NO₃)₂ stock solution (40% Pd, Merck) in 15% HNO₃, (Perkin-Elmer, Part No. BO190635). Chemical modifier solutions Mg (NO₃)₂ (Acros) and NH₄H₂PO₄ (Aldrich) were prepared from the dissolution of these salts in 1% HNO₃ medium or in DMF. Pb reference analytical solutions were prepared by successive dilutions of the respective standards for atomic absorption (Merck).

Characterizations: For preliminary analyses, a scanning electron microscope (SEM), from the Zeiss brand, model EVO LS15, was used to identify the structure of the sample. For the analysis, the samples were ground without chemical treatment for better visualization of the details of the structure of the samples from the CRT glass parts. Resolutions of 5000x, 2000x, 500x and 200x were used. Before that, the samples were metallized by a Quorum metallizer, model Q150 TE, with a thin layer of gold, favoring the SEM images, obtaining a three-dimensional image. For the treatment of the samples, a Milestone microwave oven, model ETHOS 1, equipped with high-pressure Teflon bottles and sensors for monitoring temperature and pressure was used. Flame Atomic Absorption Spectrometer (Varian, Spectra AA-55B), radiation source used was a hollow cathode lamp (HCL) (Varian). The atomic absorption spectrometer with electrothermal atomization in a graphite furnace (Aanalyt 600, Perkin-Elmer) used was equipped with a longitudinal Zeeman background corrector, an autosampler (model AS-800) and a standard THGA graphite tube with a L'vov integrated with transverse heating). As a source of radiation, hollow cathode lamps (HCL) were used to determine Pb ($\lambda=283.3$ nm, $i = 10\text{mA}$). Measurements were performed in units of integrated absorbance (integration of the transient absorbance signal as a function of time). Analytical measurements for determining the inorganic composition of the matrix, cathode ray tube glasses, were carried out in a Perkin-Elmer inductively coupled plasma optical emission spectrometer (Optima 3000 DV model), equipped with a segmented solid state detector (SCD, Segmented Array Charge Coupled Device), 40 MHz radio frequency source, peristaltic pump, crossflow nebulizer coupled to a Scott-type double-step nebulization chamber and removable quartz torch with an internal diameter of 2 mm. Purging gas (N₂) was used perpendicularly to the plasma in order to remove the lower temperature region. The equipment was operated in the axial configuration for most analytes, except for Na, K and Ca, for which the radial configuration was used. Pure argon (99.996%, White Martins) was used for analytical measurements.

Preparation of samples for spectroscopic analysis: The glass samples were subjected to different types of preparation for further analysis. The procedures will be discussed below, among them are microwave-assisted acid digestion and Pb extraction/leaching. Microwave assisted digestion and glass sample extraction (CRTs) **Method 1** – CRT glasses (microwave radiation-assisted digestion): about 125 mg of the glass sample were added in a PTFE bottle. Then 2.4 mL of HCl were added; 1.2 mL of HNO₃; 2.4 mL HF and 2.0 mL H₂O. The resulting mixture was subjected to the following heating program: Step 1: 7 min/ 500 W and Step 2: 7 min/ 550 W, Step 3: 5 min/ 600 W, Step 4: 5 min/ 630 W and Step 5: 5 min/ 0 W. At the end of the digestion, the digests were diluted with deionized water up to 50 mL. Adaptation of the methodology developed by Zachariadis et al. [10]

Method 2 – CRT glasses (microwave radiation-assisted digestion): about 125 mg of the glass sample were added in a PTFE bottle. Then 2.4 mL of HCl were added; 1.2 mL of HNO₃ and 2.4 mL of HF. The resulting mixture was subjected to the following heating program: Step 1: 7 min/ 500 W and Step 2: 7 min/ 550 W, Step 3: 5 min/ 600 W, Step 4: 5 min/ 630 W and Step 5: 5 min/ 0 W. At the end of the digestion, the digests were diluted with Milli-Q water up to 50 mL. Adaptation of the methodology developed by Zachariadis et al. [10]

Method 3 – CRT glasses (Extraction using ultrasound): about 250 mg of glass sample of CRT (fraction with smaller particle size) in 10 mL of aqueous solution 0.1 mol L⁻¹ of HNO₃ were subjected to ultrasonic radiation for a period of 1 h using an ultrasonic bath. The vial containing the sample was placed approximately 15 cm from the bottom of the bath.

Method 4 – CRT glasses (Extraction): about 250 mg of CRT glass sample (fraction with smaller particle size) in 10 mL of 0.1 mol L⁻¹ HNO₃ aqueous solution was analyzed directly, without previous treatment. For the extraction experiments, an ultrasonic bath was used (Ultrasonic Cleaner, model 1400 SC, with a frequency of 40 kHz and power of 120 W). Digests were determined by GFAAS.

Pb leaching using the ABNT 10005:2004 standard: For lead leaching from CRT samples, the ABNT 10005:2004 standard was used. This standard establishes the requirements for obtaining leached extract from solid waste, aiming to differentiate waste classified by ABNT NBR 10004 as class I (hazardous) and class II (non-hazardous). To obtain the leached extract, preliminary determinations were carried out, where all samples were evaluated to determine the extraction solution that was used in the procedure. The determination of the extraction solution that would be used in the experiment was carried out as follows: (1) 1 g of ground residue was weighed and placed in a beaker and (2) 19.3 mL of distilled water was added, covered with paper and stirred for 5 min. The pH was measured and it was ≤ 5.0 , thus indicating that the extracting solution that should be used in the tests was the first extraction solution. The preparation of extracting solution number 1 was carried out as follows: 5.7 mL of glacial acetic acid was added to distilled water, followed by the addition of 64.3 mL of 1.0 M NaOH. The volume was completed to 1L. The pH of this solution was (4.93 ± 0.05) . After the test to determine the extracting solution, the procedure for lead leaching was carried out. For this, approximately 1 gram of each sample was weighed and 19.3 mL of deionized water was added, covered with a watch glass and the mixture was stirred vigorously for 5 min with a magnetic stirrer. This procedure was applied to samples of soils and CRTs. After checking the pH of the samples, which were $\text{pH} \leq 5$ (Table 5), 20 mL of extracting solution n°1 was used. Then, the samples were placed in a Dubnoff Bath under agitation for 18 hours at a temperature of 27°C.

RESULTS AND DISCUSSION

Determination of pb in glasses from CRTS

Determination of concentration of toxic elements by Energy Dispersive X-Rays (EDS): The value found for lead by EDS (Table 2) was higher than that established by Directive 2002/95/EC for waste electrical and electronic equipment (0.1% m / m). Lead (Pb), barium (Ba) and strontium (Sr) are usually found in cathode ray tubes. Glasses containing lead are funnel and neck, while elements such as barium and strontium are found in TV monitor screens. Generally, the composition of waste CRT glasses consists of lead oxide, which represents 21-24% by weight (Pb: 2.4-2.7% atomic mass) in the funnel, while the concentration of Ba and Sr oxides reaches the figure of 9 to 13% by weight (Ba: 1.4-1.6% atomic mass) and 1-2% by weight of (Sr: 1.5-2.1% - atomic mass), respectively [11]. According to Andreola et al. [12] It is estimated that approximately 65% of the weight of a television set or a computer monitor consists of cathode ray tube (CRT), and is composed of 85% glass (65% panel and 30% and 5% glass funnel neck).

Table 2. Concentration of Pb, Ba and Sr in a CRT sample by EDS

CRT components - Television (A) and computer (B)	Weight of Elements (% - m/m)					
	Ba		Pb		Sr	
	A	B	A	B	A	B
Canhão de elétrons	--	--	24.93	25.58	--	--
Neck	1.57	--	16.88	16.56	--	--
Funil	1.67	--	19.91	15.95	--	--
Tela	6.05	7.92	1.98	--	5.47	5.88

CRT glass analysis by GFAAS: The optimizations of the GFAAS heating programs for the glass sample from a color CRT monitor were conducted in two different media: 1) in the aqueous solution of the glassy sample after digestion assisted by microwave radiation in an acid medium and 2) in the suspension obtained after sonication of the sample in 1% HNO₃ medium. For this, the conventional univariate method was used, where the conditions recommended by the manufacturer and the potential of chemical modifiers on the matrix were evaluated independently, through the construction of pyrolysis and atomization curves. In both media the samples were diluted 200 times. Sensitivity, background signal and minimum atomization temperature (to increase graphite tube lifetime) were criteria for selecting the best conditions. The pyrolysis and atomization curves in the absence and presence of chemical modifier for Pb in the digested solution and in the suspension (extraction) in the presence and absence of chemical modifier are shown in Figure 1 and 2.

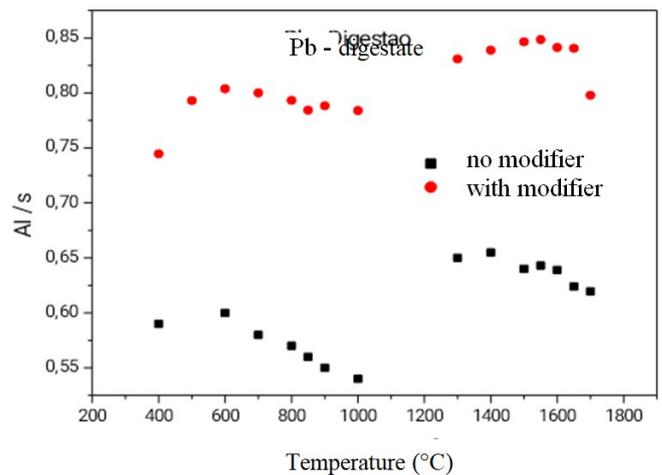


Figure 1. Pyrolysis and atomization curves for Pb in the digestate

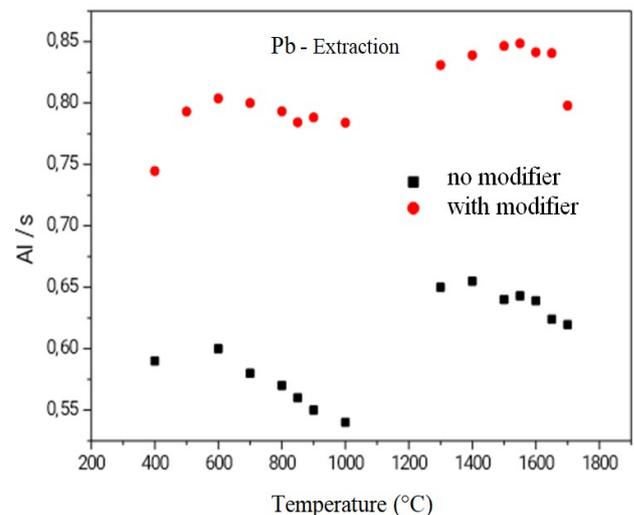


Figure 2. Pyrolysis and atomization curves for Pb in the suspension from the extraction

From the pyrolysis and atomization curves in the two media investigated, pyrolysis temperatures of 850 and 800°C were chosen for the digestate and the suspension, respectively, and atomization temperatures of 1600 and 1850°C for the digestate and for the suspension, respectively. These values were chosen considering the sensitivity, the background signal and the minimum atomization temperature (to increase the lifetime of the graphite tube). Lead is a volatile element that generally undergoes losses in tubes with transverse heating (THGA) at temperatures above 500°C in the absence of a chemical modifier, as can be seen in the pyrolysis curves obtained, hence the need to use a chemical modifier to reduce Pb volatility in the analyzes in question. The optimized instrumental conditions were used in the preliminary study for the determination of Pb in glasses from CRT (screen and cone, 2:1 ratio) in order to evaluate the two initially proposed methods. The analytical characteristics were determined using the optimized conditions for each element. The limit of detection (LOD/ $\mu\text{g L}^{-1}$) and the limit of quantification (LOQ/ $\mu\text{g L}^{-1}$) were calculated using the equations $\text{LOD}=3 \times \text{S}_{\text{Branco}}$ and $\text{LOQ}=10 \times \text{S}_{\text{Branco}}/b$, where S_{Branco} is the standard deviation of ten blank measurements and b , the slope of the calibration curve. Sensitivity was expressed by the amount of analyte that results in an analytical signal of 0.0044 absorbance units (characteristic mass). The analytical characteristics for the two investigated methods are presented in Table 3. Analytical curves were obtained with analyte addition in the range of 20 - 100 mg/L.

Addition and recovery studies were performed on samples doped at three concentration levels. Optimized conditions were applied to the four proposed sample preparation procedures. The recovery values obtained for the different procedures and the concentration levels (in which the samples were doped) are presented in Table 4. From the recovered values obtained, it is possible to make a comparison between the different sample preparation procedures investigated. The results indicated that the two digestion methods assisted by microwave radiation did not present a significant difference when the t test was applied in relation to the recovery values. Both methods presented recovery values considered quantitative, that is, close to 100%, which can then be applied in the determination of Pb in CRT glasses. Regarding the extraction method using ultrasound, the recovery values obtained were semi-quantitative, and the direct method without the use of ultrasound showed lower recovery values. This indicates that method 3 can only be used for semi-quantitative determinations in CRT glasses and method 4 is not suitable for the determination of Pb in the aqueous solution resulting from the extraction by simple homogenization of the sample. The estimated concentration value for the investigated sample (method 1) from the quantification using the analyte addition method was $735.52 \pm 6.12 \text{ mg kg}^{-1}$ and $886.61 \pm 5.49 \text{ mg kg}^{-1}$, for the mixture of glass from the television (A) and computer (B), respectively, indicating that this type of glass, according to the Environmental Protection Agency (EPA), is considered toxic waste.

Table 3. Analytical characteristics for the determination of Pb in a glass sample of digested CRT and in the solution from the extraction

Parameter	Digested	Extraction
Range of work ($\mu\text{g L}^{-1}$)	20-100	20-100
R^2	0.99223	0.9898
LOD (mg L^{-1})	2.1	2.4
LOQ (mg L^{-1})	6.9	7.9
characteristic mass	32.8	33.7
Recovery (%)	104-107	85-93
Precision (%)	3.1	4.6

Table 4. Recovery values obtained for different procedures and concentration levels

Method	Concentration Level mg L^{-1}	Recuperação (%)
1. Microwave acid digestion in the presence of water.	25	104
	50	105
	75	107
2. Microwave acid digestion without water.	25	106
	50	98
	75	104
3. Solution from extraction with 1h of sonication.	25	88
	50	85
	75	93
4. Solution from extraction without sonication.	25	78
	50	81
	75	82

Table 5. Results of Pb analyzes in the extract leached by FAAS

Samples	TV		PC	
	mg/L	mg/kg	mg/L	mg/kg
Electron Cannon	48.22±0.39	964.44±7.86	50.2±0.25	1004.10±4.95
Neck	27.10±2.05	541.33±41.10	31.8±2.40	634.65±4790
Funnel	19.28±1.03	379.70±16.82	33.06±1.35	658.75±25.29
Screen	3.28±0.29	65.56±5.73	1.30±0.11	25.95±2.22

Table 6. Results of the analysis of Pb in the extract leached by FAAS in the mixture (proportion of electron gun, neck, funnel and screen: 1:1:1:4)

Sample	Concentration (mg/L)	Concentration (mg/kg)
CRT mixture A	31.90±0.70	638.00±14.00
CRT mixture B	33.49±2.77	668.72±54.78

Table 7. Results obtained for the analysis of Pb in the extract leached by ICP OES.

Sample	TV		PC	
	mg/L	mg/kg	mg/L	mg/kg
Electron Cannon	50.42±1.29	1004.89±25.80	51.68±1.11	1032.25±22.08
Neck	30.73±0.68	613.99± 13.59	27.22±0.68	617.39 ± 13.61
Funnel	18.11±0.43	361.70±8.55	20.91±0.51	417.67± 10,20
Screen	2.57±0.17	65.31±3.37	2.49±0.11	29.72±2.15

According to the Agency, this type of waste (CRT) should be recycled to avoid environmental problems. [12]

Determination of Pb in CRT leached extract by FAAS: The results obtained in the analysis of Pb in the extracts leached by FAAS are presented in Table 5. The analysis of the mixture of the components of the CRT was also carried out, being that, generally, it is in this form that the residue appears in the environment. The results obtained are shown in Table 6.

Determination of Pb in the leached extract of CRTs by ICP OES: The samples of the CRT components (electron gun, neck, funnel and screen) submitted to the extraction test according to the ABNT NBR 10005:2004 b standard were analyzed by ICP OES (Table 7). Analyzes were performed in triplicate. Again, the analysis of the mixture of components was carried out. The results obtained are shown in Table 8.

Table 8. Results obtained for the analysis of Pb in the leachate extract analyzed by ICP OES in the mixture (proportion electron gun, neck, funnel and screen: 1:1:1:4)

Sample	Concentration (mg/L)	Concentration (mg/kg)
CRT mixture A	32.61±0.43	650.83±8.67
CRT mixture B	21.09 ± 0.60	621.02±11.90

The results obtained for Pb in the CRT leached extract show that the analyzed samples presented high concentrations, which according to ABNT NBR 10004:2004 the samples are classified as hazardous waste class 1, that is, the concentrations exceeded the allowed limit of 1, 0 mg/L. The hazard of glass can be determined using the Toxicity Characteristic Leaching Procedure (TCLP) (SW-846 Method 1311; USEPA 2003), which determines the toxicity of waste through leaching. That is, the waste has toxic characteristics if the concentration of any contaminant regulated in the TCLP is higher than established. According to the regulations of the US EPA, the limit established for lead by the TCLP corresponds to 5.0 mg/L. [13,14] The two methods investigated for analysis of the leachate extract (FAAS and ICP OES) agreed with each other for most measurements with 95% confidence when Student's t test was applied. Tables 7 and 8 show the concentrations of lead in mg/kg compared to the results of Directive 2002/95/CE, concerning the restriction of the use of certain hazardous substances in electrical and electronic equipment, we can consider that only samples of CRTs of the electron gun exceed the established limit (0.1% m/m) the other samples are within the established limits.

Analytical characteristics of the developed methods: Table 9 presents the analytical characteristics for the different methods for the determination of Pb by FAAS, GFAAS and ICP OES. The analytical characteristics were determined using the element's optimized conditions. The limit of detection (LOD/ $\mu\text{g L}^{-1}$) was calculated using the equation $\text{LOD}=3 \times \text{S(White)} / b$, where S(White) is the standard deviation of ten blank measurements and b, the coefficient of the calibration curve.

Table 9. Analytical characteristics for lead calibration curve for CRT samples (glass)

Technique	Range of work (mg/L)	wavelength (nm)	R ²	LOD (mg/L)
ICP OES	0.0 – 50.0	217.0	0.999	5.32
FAAS	0.0 – 50.0	217.0	0.941	6.50
GFAAS EXTRACTION	20.0 -100.0	217.0	0.9898	2.40
GFAAS - DIGESTION	20.0 –100.0	217.0	0.99223	2.10

The limits of detection (LOD) obtained by GFAAS were lower than the limits obtained using ICP OES and FAAS techniques. In this case, the GFAAS technique showed better sensitivity.

CONCLUSION

The results obtained for the vitreous samples, the two digestion procedures assisted by microwave radiation are adequate for the determination of Pb in CRT glasses, and the extraction procedure using ultrasound can only be used for semi-quantitative determinations of Pb in this type of sample. From method 1, digestion assisted by microwave radiation, it was also possible to verify that the investigated CRT glass samples are considered as toxic waste, according to the Environmental Protection Agency (EPA), that is, they exceeded the limit of 5, 0 mg L⁻¹. The total concentration of Pb in the CRTs were 735.52 ± 6.12 mg kg⁻¹ and 886.61 ± 5.49 mg kg⁻¹ for the mixture of glasses from the television (A) and computer (B), respectively. For the leaching tests, about 85% of the Pb present in the residue was extracted from the samples. The two methods investigated for leachate analysis by FAAS or ICP OES were suitable for Pb determination. The leaching tests carried out for the CRT residues reached Class I values (hazardous waste) in accordance with the ABNT NBR 10004:2004 standard.

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