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CHEMICAL ANALYSIS OF POTENTIALLY TOXIC ELEMENTS PRESENT IN THE ACTIVE MATERIAL OF BATTERIES

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ABSTRACT

This study develops an analysis procedure to determine potentially toxic metals such as chromium, cadmium, nickel, and lead in the active material of batteries and cells by atomic absorption spectrometry (FAAS) and inductively coupled plasma optical emission spectrometry (ICP OES). The characterization of the active material was performed by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and x-ray diffraction (XRD). The analysis procedures with the active material were used to extract metals, following the ABNT NBR 10.005/2004 procedure in comparison with the acid mineralization of the material in a microwave oven using aqua regia with and without the addition of hydrogen peroxide. The results of the characterization provided the obtaining of the particle size, morphology, and the constituent compounds of the active material. The leaching assay proved to be adequate for promoting an extraction of 85-95% of the analytes when compared to the values of total digestion. The accuracy of the proposed method was evaluated by addition and recovery test with results in the range of 95-108%. The concentrations obtained from the analytes investigated by acid mineralization were 5 to 15% higher than the leached extract. The concentrations of Cr, Cd, and Pb are above the value established by the current legislation, classifying them as hazardous waste.

Keywords: Batteries. Potentially toxic metals. FAAS. ICP OES.

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INTRODUCTION

Given the growing production of electrical and electronic equipment (EEE) to meet technological innovation and expansion in the market, which caused the reduction of the useful life of many equipment powered by batteries and batteries. Where they became obsolete in a short time, and as a consequence the generation of Waste Electronic Electrical Equipment (WEEE), which leads to a significant increase in this waste and used batteries and batteries after reaching the end of their useful life, which are improperly disposed of in common household waste [1].

Data According to the Brazilian Association of the Electrical and Electronics Industry (ABINEE, in Brazil in 2014, the sale of cell phones was 10.7 million units in the first two months of the year, and of this total, 3.9 million traditional devices and 6.8 million smartphones were sold [2].

Battery components contain valuable and potentially toxic metals (Pb, Cd, Hg, As, Cr, Cu, Zn, Mn, Ni, and Li) as well as harmful substances that cause environmental and human problems when disposed of improperly. [15-17].

These metals are bioaccumulative because when any of these elements is absorbed by the human body in high concentrations, they cause damage to their structure, penetrating cells and altering their normal functioning, with inhibition of enzymatic activities. Thus, the toxicity of a metal is related to the availability of the chemical form that this metal is in the environment and also to the routes of introduction that can be through inhaled air, orally, or dermally [18].

The main risks of contamination for the environment are related to the disposal of solid waste in landfills, resulting from the leaching process. And when percolation occurs, the waste comes into contact with water, either as a reagent or as a solvent, which is a main agent for weathering to occur, as well as other chemical and physical processes, which come into contact with the waste material, where each of its constituents dissolves at a finite rate [4,5].

In recent decades, the great concern for the environment has resulted in stricter regulations around the world regarding the proper disposal of hazardous waste such as batteries and batteries that contain toxic metals [1].

Brazil was the first country in Latin America to regulate the disposal of batteries. Through CONAMA Resolution No. 401 of November 4, 2008. The regulation establishes the maximum limit of lead, cadmium and mercury for portable, button and miniature batteries and cells (zinc-manganese and alkaline manganese) that must contain: up to 0.0005% by weight of mercury, up to 0.002% by weight of cadmium and traces of up to 0.1% by weight of lead; as well as the criteria and standards for its environmentally appropriate management. Manufacturers and establishments that sell batteries must receive them from consumers, after use through collection points, to be recycled, treated, or disposed of in an environmentally safe way [11, 19].

The Brazilian Standard ABNT NBR 10.004/2004 "Solid Waste – Classification" aims to identify a process or activity that gave rise to the waste, as well as its constituents and its characteristics, when compared in a list of waste and substances that cause the impact on health and the environment, in the aforementioned standard [58]. Batteries and cells have hazardous characteristics of waste, given toxicity, classifying them as hazardous waste (class I) according to the aforementioned annexes C and F of this standard, in which the inorganic parameters are presented, that is, the concentration - Maximum limit in the leached extract, for Cd up to 0.5 mg L-1, Pb 1.0 mg L-1, Total Cr 5.0 mg L-1, and Hg 0.1 mg L-1. [20]

In sequence, ABNT NBR 10.005/2004 [21], deals with the procedures for obtaining the leached extract from solid waste, and it is possible to classify the residue given the results obtained by the procedure to obtain the leached extract, and compare the values of the concentration - Maximum limit of the extract obtained in the leaching test of NBR 10.004/2004 [20].

Federal Law No. 12,305/10, which establishes the National Solid Waste Policy (PNRS), provides the principles, objectives, and instruments for solid waste management, determining an action plan for generating companies, states, and municipalities [1,22].

The main instrument of the PNRS is the prevention and reduction of waste generation, with proposals for sustainable consumption, increased recycling, and the reuse of solid waste in order to obtain an environmentally appropriate destination. Thus, it establishes to generators and consumers a series of responsibilities for industries, characterized by a set of actions, procedures and means to collect and return waste to the generating companies, obtaining reuse in its life cycle or other production cycles from the generation and disposal of the waste generated by it, resulting from the inadequate management of solid waste. Reverse logistics is a priority for waste such as pesticides, batteries, tires, and others as provided for in article 33 of the aforementioned law [22, 23].

As an international legislation, the European Union introduced Directive 2006/66/EC of 6 September 2006, whose main objective is to minimize the negative impacts of batteries on the environment, contributing to the protection, preservation and improvement of the quality of the environment, establishing limits for the amount of hazardous substances, prohibiting batteries containing metal content above [7,11]: 0.0005% by weight of mercury; 0.002% by weight of cadmium; 0.004% by weight of lead.

Directive 2002/96/EC of 27 January 2003 – On Waste Electrical and Electronic Equipment (WEEE) aims at the prevention of electrical and electronic equipment, the reuse, recycling and other forms of recovery of such waste, to reduce the amount of waste to be disposed of. The Directive shows us which equipment belongs to the WEEE category in its Annex I, in which mobile phones fall under computer and telecommunications equipment [6].

Few extraction methods in the literature simulate the leaching of these elements. Studies present the hydrometallurgical processes, which have been used on a large scale because they present an efficient method in the separation of battery components with the recovery of valuable and toxic metals based on physical and chemical processes. Thus, physical processes involve mechanical and thermal processes that separate coarse components from the active material (cathode and anode) and chemical processes that involve acid leaching followed by the purification step, solvent extraction, electrochemical process, and chemical precipitation. [1, 3,11].

Currently, the use of analytical methods using acid mineralization with the use of the microwave oven as an energy source for the mineralization of samples has been used by some studies [14,24,25], thus presenting an alternative about conventional procedures, since it reduces the time of sample preparation and associated problems such as the loss of volatile components and lower levels of contamination of the material, also using a smaller volume of reagents for the procedures. [8,9,10]

The present work consisted of two stages. The purpose of the first stage was to characterize the active material of the batteries to identify the morphology and the grain size and verify the presence of chemical elements and compounds. As a second step, different procedures were applied to develop a chemical analysis procedure to determine the potentially toxic metals in the active material applying a method of metal extraction and acid mineralization using a microwave oven, where the samples were analyzed by FAAS and ICP OES. The data obtained allowed the evaluation of the most accurate and efficient procedure for the determination of metals.

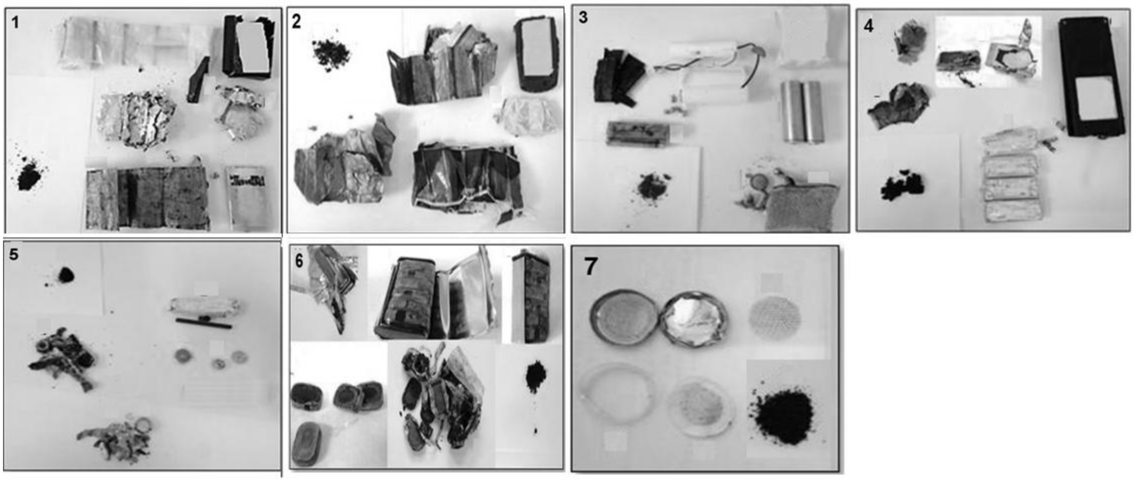
EXPERIMENTAL

COLLECTION, CLASSIFICATION, AND DISMANTLING OF MATERIAL

Batteries were collected through collection points at the university itself and in an electronics store where they were discharged, and thus they were separated and classified according to type, origin, and use.

The battery samples were dismantled (Figure 1) manually and their components such as metal housing, internal plastic, external plastic, paper, external circuit, cathode support, and anode were separated. The powder components (cathode + anode + electrolyte) of each battery and cell were separated, corresponding to the "active material" mentioned in this work.

Figure 1: Dismantling and Battery components. 1- Li-ion Battery, 2-Polymer Li-ion Battery, 3-NiCd Battery, 4-NiMH Battery, 5-AAA Cylindrical Battery, 6-Heavy Duty Battery, 7- Button Battery



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EQUIPMENT

ZEISS EVO LS15 scanning electron microscope with 10 and 20 kV electron beams and with the coupling of an Oxford Instruments INCAX-act for X-ray energy dispersive analysis. The images were taken at a magnification of 100x, 1000x and 5000x, for all samples and were analyzed using the Image J program, to obtain the average particle size, performed by manual counting.

X-ray diffractometer (SHIMADZU- XDR- 6000- LABX) using Kα-Cu radiation (λ = 1.5418 Ǻ), with the following parameters: velocity of 1°/minute, reading interval 0.02° and with angle interval 2θ between 5° and 80°. The diffractograms were analyzed using the X'Pert HighScore program, from Philips Analytical B.V., 2001.

Perkin-Elmer spectrometer (Optima 3000 DV model), equipped with a segmented array charge coupled device (SCD) detector, 40 MHz radio frequency source, peristaltic pump, crossflow nebulizer coupled to a Scott-type double-step nebulization chamber, and a detachable quartz torch with an internal diameter of 2 mm. Purge gas (N2) was used perpendicular to the plasma to remove the region of lower temperature. The equipment was operated in the configuration (axial or radial) for all analytes, pure argon (99.996%, White Martins) was used in the analytical measurements. The analytical signals obtained in ICP OES were expressed in emission intensity (peak area).

FAAS atomic absorption spectrometer of the brand: Varian, model: Spectra AA-55B. The radiation source used was an HCL (Varian) hollow cathode lamp.

REAGENTS

All chemical reagents used were of high degree of analytical purity. Deionized water in GEHAKA water purifier system with conductivity of 0.35 μS/cm.

For the calibration curves, ultra-pure water (resistivity 18.3 MΩ cm) obtained by the Mega Purity system and nitric acid distilled in a sub-boiling system were used.

The standard solutions for the calibration curve for the analysis of FAAS and ICP OES were prepared from dilutions of the salt ampoules of the elements (Cr, Cd, Hg, Ni, Pb and As Tritisol, Merck), with distilled nitric acid 1% v/v (Merck).

All the glassware and jars used were washed with water and neutral detergent and, subsequently, immersed in 10% v/v nitric acid solution for 24 hours and rinsed with deionized water before use.

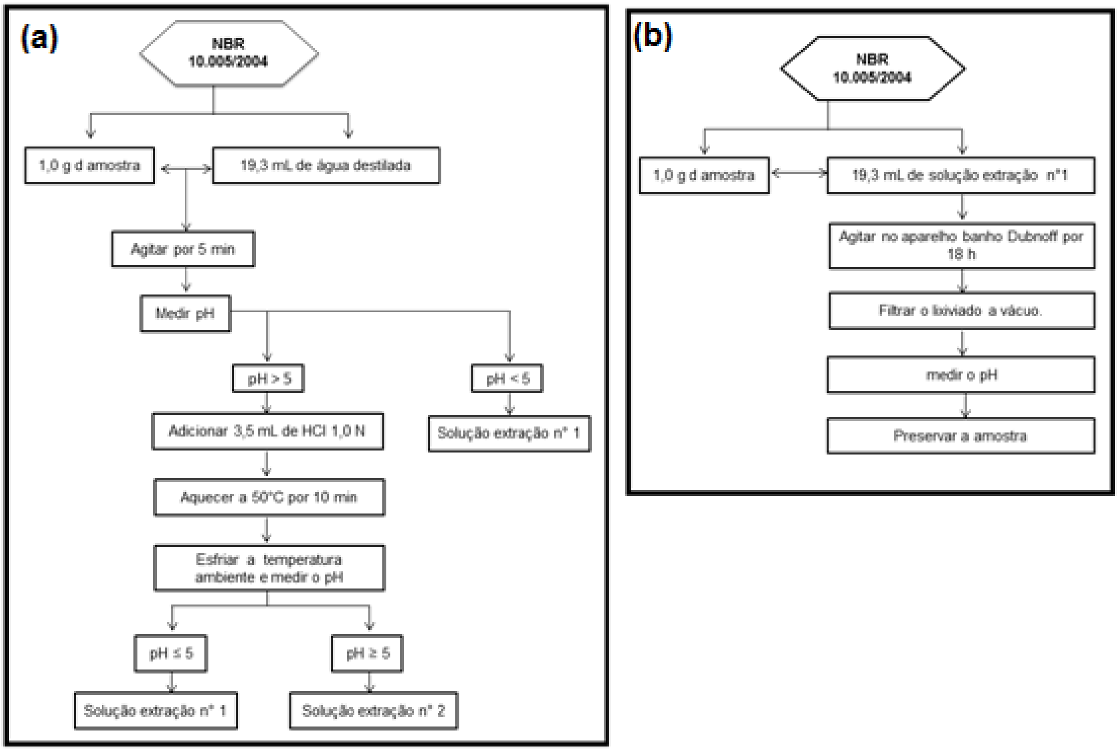
SAMPLE PREPARATION PROCEDURES

LEACHING TEST

To identify the potentially toxic metals present in the battery samples, the leaching test was performed according to ABNT NBR 10.005/2004.

The procedures performed for the determination of the extraction solution and the procedure for the leaching test are shown in figure 2.

Figure 2: (a) Procedure for the determination of the extraction solution. (b) leaching procedure for waste containing solids content equal to 100%.



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The leachate obtained was preserved in order to preserve its chemical characteristics and submitted to quantitative analysis by ICP OES and FAAS.

DIGESTION OF SAMPLES USING RADI-ASSISTED HEATING MICROWAVE ACTION

For the treatment of the samples, a Milestone microwave oven model ETHOS 1 was used, equipped with Teflon® flasks, closed high pressure and sensors for monitoring temperature and pressure, where the sample digestions were performed.

Two sample preparation procedures applied in the determination of potentially toxic metals in batteries by acid mineralization in a microwave oven were tested and compared.

The sample chosen for this test was the active material of the NiCd battery, because it contains a large amount of cadmium in its composition, and also because it is a potentially toxic metal [12]. The digestates were analyzed by ICP OES. The two procedures studied are presented below:

Procedure A: 250 mg of the active material of the NiCd battery was weighed in a Teflon® vial, and then 4.0 mL of HNO3, 4.0 mL of HCl, and 1.0 mL of H2O2 were added.

The vials with the samples and the acid mixture were submitted to the microwave oven heating program described in Table 1. After digestion, the samples were transferred to falcon centrifuge tubes and avolumated to 50 mL. This procedure has been adapted from the microwave oven manual and literature [25, 26-28].

Table 1- Microwave program using 6 Teflon® vials for digestion of the active material of the NiCd battery

Steps	Temperature (°C)	Time (min)	Pressure (bar)	Power (W)
1	130	5:00	40.0 bar	500 W
2	130	2:00	40.0 bar	500 W
3	170	2:00	40.0 bar	500 W
4	170	2:00	40.0 bar	500 W
5	200	3:00	40.0 bar	500 W
6	200	15:00	40.0 bar	500 W

Source: Author himself

Procedure B: 100 mg of the active material of the NiCd battery was weighed in a Teflon ® bottle, 8.0 mL of aqua regia was added and left to rest for 18 hours, due to the acid mixture (aqua regia) gradually decomposing with the release of reactive agents. The flasks containing the samples and the acid mixture were subjected to the microwave oven heating program described in Table 1. After digestion, the samples were transferred to falcon centrifuge tubes and avolumated to 50 mL. This procedure was an adaptation of the procedure recommended by the microwave oven manufacturer and the literature [26-28].

To evaluate the accuracy of the method, procedure B was chosen and the test of addition and recovery of analytes with three levels of concentration in the NiCd battery sample was performed. The amount of sample weighed to perform the procedure was 50 mg, which is lower than that used for procedure B, due to the high concentrations obtained of the element cadmium, and it is necessary to reduce the amount of active material to be analyzed to avoid sudden dilutions.

Weigh 50 mg of the active material in a Teflon ® vial and add to the standard solutions (three concentration levels), with another 1.6 mL of deionized water. The vials were partially closed and the solution remained at rest for 12 hours. After this period, 8.0 mL of aqua regia were added, and the samples remained at rest for another 18 hours. This test was performed in duplicate. The flasks containing the sample and the acid mixture were subjected to the microwave oven heating program described in Table 1, changing only the power to 1000W. They were then transferred to falcon centrifuge tubes and bulked to 50 mL. Analytical measurements were performed by ICP OES and FAAS.

Procedure B was applied to the other cell and battery samples and the digested ones were analyzed by ICP OES and FAAS.

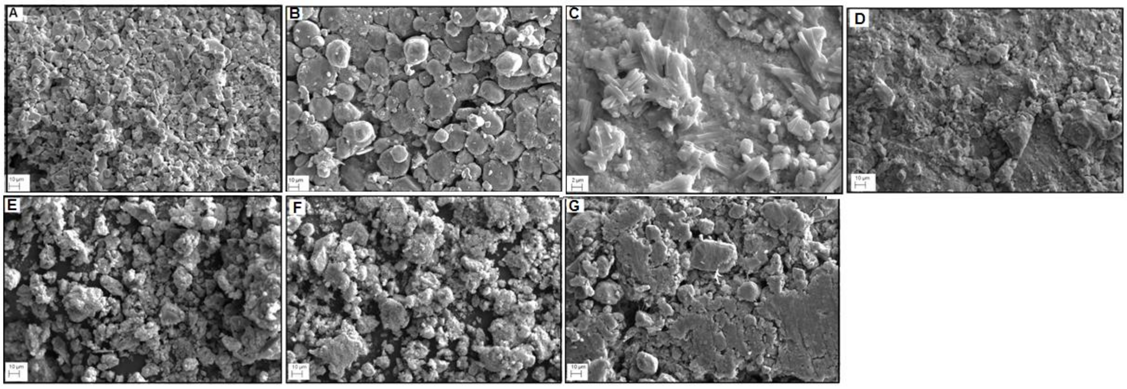
RESULTS AND DISCUSSION

CHARACTERIZATION OF THE ACTIVE MATERIAL

Through the micrographs of the active material of the battery samples, it was possible to notice: different morphologies (globular shape, spherical, flakes, granules), elemental composition, as well as an agglomeration of particles resulting from the probable presence of moisture in the samples and to obtain the average size of the particles, which was calculated using the Image J program.

The particle size ranged from 0.008 to 0.023 mm (figure 3), which interferes with the best leachate extraction result, because the smaller the size, the easier it is to dissolve and the greater the leaching efficiency. Thus, in order to meet the requirements of NBR 10.005/04, the results obtained by SEM for the particle size of the active material of batteries were less than 9.5 mm.

Figure 3- Micrographs obtained by SEM of the active material of batteries and cells at 1,000x magnification.



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By the EDS spectra, the elemental composition (% weight) found in the active material for the different battery samples as:

- Li-ion: the presence of 0.23% Aluminum and 53.07% Cobalt;
- Li-ion polymer with 11.43% Cobalt and 0.17% Copper and 2.0% Fluorine;
- NiCd with 50.50% Cadmium and 0.62% Nickel;
- NiMH with 1.03% Aluminum, 5.32% Cobalt, 42.57% Nickel and 3.37% Zinc;

- Zn-C battery with 0.23% Carbon, 0.12% Potassium, 0.19% Calcium, 14.74% Manganese, 31.86% Oxygen, 1.13% Iron, 5.56% Zinc, 0.33% Magnesium, 0.67% Aluminum, 3.96% Chlorine, and 1.22% Silicon.
- Zn-C Heavy Duty Pile with 3.65% Chlorine, 0.90% Potassium, 12.10% Carbon, 17.63% Oxygen, 56.39% Manganese, 8.61% Zinc, 0.60% Aluminum, 0.13% Silicon.
- Lithium Button Battery with 0.92% Chlorine, 22.46% Carbon, 32.24% Oxygen, 33.34% Manganese, 0.13% Chromium, 0.45% Iron, 10.31% Fluorine and 0.15% Sodium.

The results of SEM with EDS indicated the presence of a potentially toxic metal (Cd) only in the NiCd battery, where Cd is present in high concentrations with 50.50% by weight of this element, in which it presents an amount above that established by current legislation.

For the other toxic metals found in the EDS spectra, in smaller quantities such as Cu, Zn, Mn, Cr and Ni where they are not controlled by current legislation, because these metals are essential to the proper functioning of living organisms in the form of traces and because they are bioaccumulative they are harmful to all types of life when in high concentrations or in certain chemical combinations as well as in the chemical form in which the metal is found in the environment [18].

X-RAY DIFFRACTION STUDIES

Through the diffractograms obtained for each sample, it was possible to compare them with the reference charts of the X'Pert HighScore program and with the literature consulted, the peaks coming from the possible constituent compounds of the active material of the samples.

For the Li-ion battery, it was possible to perceive in the diffraction peaks with the predominance of the following compounds: LiCoO2, Li0.63CoO2 and C, as confirmed in the investigated literatures [17, 29-31].

Li-ion Polymer battery, the presence of well-defined diffraction peaks characteristic of the compounds: LiCoO4, LiPF6, LiAl(PO4)F and C was observed, as confirmed in the investigated literature [17,29,31].

In the presence of well-defined diffraction peaks, characteristic of the compounds that make up the cathode - Cd(OH)2 and the Ni(OH)2 anode was observed as confirmed in the literature [13].

In the NiMH battery, the presence of well-defined diffraction peaks was observed, characteristic of the compounds that make up the cathode - Ni (OH)2 and the material that make up the electrolyte (KOH or LiOH), as confirmed in the literature [14].

Zn-C cell, it was possible to observe the presence of diffraction peaks of the compounds: (NH4)3(ZnCl4)Cl, C, Zn(OH)2, , Mn2O7, as confirmed in the literature [3,32].

In the Zn-C Heavy Duty stack, the presence of well-defined diffraction peaks characteristic of the following compounds was observed: FeCl3, FeO, Fe2O3.H2O, NH4Cl, C10H4MnO4 and Cu(OH)2.H2O

Button Cell Li, the presence of diffraction peaks characteristic of the compounds: C and LiMnO2 was observed according to the literature consulted [27].

DETERMINATION OF POTENTIALLY TOXIC METALS IN LEACHATE

In the procedure for determining the extractor solution, it was noted the release of gases in the NiCd and NiMH batteries, after the addition of the hydrochloric acid solution at 1.0 mol. L-1, this fact occurs due to the reaction of the acid with the active material.

Given the results of the second pH measurement (pH ≤ 5.0) in all samples, it determined the use of extractor solution n°1 (acetic acid + sodium hydroxide) to perform the leaching assay, in which this extractor solution has properties to dissolve the metals in the solution.

After determining the extractor solution, the leaching test was performed. The leached extracts of the active material of the batteries were analyzed by FAAS and ICP OES.

The detection limits, defined as three times the standard deviation of the lowest standard measurements for FAAS and ICP OES were (mg. L-1): Cr 0.01 and 0.01; Cd 0.01 and 0.01, Ni 0.29 and 0.01, Pb 0.11 and 0.01.

The concentrations of toxic metals in the leached solutions of the determined battery samples are presented in Table 3.

Table 3 - Measurements of the signal strengths of potentially toxic metals obtained in procedure A for the NiCd battery analyzed by ICP OES with axial configuration.

	Analytes (signal strength in cps)

Elements	Cr	CD	Nu	Pb
Wavelengths (nm)	205.56 (II)	214.44(II)	232.00(I)	220.35(II)
Procedure. The	6554	2699724	13510	3253
Procedure. B	6415	1342802	8872	3164

Author himself

With the use of the ICP OES technique, it showed the following characteristics: high sensitivity, wide dynamic linear range, high precision and accuracy and low detection limits. Horizontally oriented plasma – axial, showed higher sensitivity and lower detection limits when compared to plasma oriented in the radial position.

In the ICP OES technique, despite the good quality of the analytical calibration curve (R2) containing only arsenic (As) and mercury (Hg) in aqueous solution, a good definition of emission peaks was not obtained in the matrices analyzed. This behavior was expected, because the ICP OES technique is less suitable for the determination of more volatile elements (such as: arsenic, bismuth, germanium, indium, lead, antimony, selenium, tin and tellurium), which are better analyzed by hydride generation atomic absorption spectrometry (HG AAS) for arsenic (As) and cold vapor atomic absorption spectrometry (CV AAS) for mercury (Hg).

When the results of FAAS and ICP OES are compared to the results obtained by EDS, it is possible to verify that EDS does not have adequate sensitivity to analyze this type of sample, as it was only possible to detect Cd in the NiCd battery.

Given the results obtained in table 2, the NiCd battery has a high concentration of Cd in its composition and is considered a toxic waste according to the ABNT 10.005/2004 standard. Other metals such as Cr and Pb were also found in the investigated samples, indicating that the presence of large amounts of this type of waste can cause leaching of these metals into the soil and contaminate the environment.

Table 2 - Concentration of potentially toxic metals present in the active material of the leached extract, analyzed by FAAS and ICP OES with axial configuration**.**

Analytes (mg/Kg)								
Elements	**Cr**		**CD**		**Nu**		**Pb**	
Techniques	**FAAS**	**ICP OES**	**FAAS**	**ICP OES**	**FAAS**	**ICP OES**	**FAAS**	**ICP OES**
Wavelength (nm)	357.90	205.55(II) b	228.80	214.44(II) b	232.00	232.00 to (I)	217.00	220.35(I) to
Batteries								
Li-ion	2.29 ± 0.81	2.39 ± 0.15	169.63 ± 0.01	173.34 ± 3.62	8.98± 0.06	8.52 ± 0.13	1.80 ± 0.01	1.78 ± 0.08

Li-ion in.	0.80 ± 0.01	0.83 ± 0.02	150.00 ± 0.29	150.22 ± 4.90	9.00 ± 0.01	9.53 ± 0.23	2.80 ± 0.02	2.80 ± 0.14
NiCd	0.91 ± 0.21	0.99 ± 0.07	2269.79 ± 32.83	2,239.79 ± 18.77	581.66 ± 78.96	582.65 ± 12.75	1.81 ± 0.32	1.83 ± 0.11
Nimh	2.13 ± 0.67	2.32 ± 0.18	39.98 ± 8.27	41.12 ± 2.98	506.50 ± 76.96	508.01 ± 14.85	1.00 ± 0.35	0.88 ± 0.10
Batteries								
Zn-C	0.80 ± 0.02	0.87 ± 0.03	93.29 ± 5.37	93.75 ± 2.45	91.95 ± 1.33	92.32 ± 2.21	1.20 ± 0.10	1.26 ± 0.11
Zn-C Heavy Duty	0.62 ± 0.15	0.67 ± 0.09	6.67 ± 1.55	7.23 ± 0.39	2.00 ± 0.02	2.17 ± 0.09	1.80 ± 0.03	1.97 ± 0.12
Li Button - ion (B)	1.47 ± 1.15	1.32 ± 0.09	19.99 ± 1.46	18.22 ± 0.71	3.33 ± 1.15	3.12 ± 0.13	4.46 ± 1.15	4.98 ± 0.12

Student's t-test was applied to verify accuracy when comparing the results of the leachate extract obtained by the FAAS and ICP OES techniques. The t-test with a 95% confidence level proved to be adequate for the determination of the analytes of interest in the leached extracts, because the results obtained through the two techniques were concordant with each other, i.e., there was no significant difference between them.

DETERMINATION OF POTENTIALLY TOXIC METALS IN DIGESTATES

To determine the total concentration of potentially toxic elements in the battery samples, a preparation procedure was developed that allowed the total digestion of these samples. Two procedures were tested to assess digestion. For this, the active material of the NiCd battery was digested using procedure A and B using microwave-assisted heating of the sample. The digestates were analyzed by ICP OES with axial configuration where it presented better sensitivity, thus allowing the best procedure to be verified.

It is possible to notice in table 3, the results of the signal intensity measurements of the toxic metals, which were obtained by the procedures of decomposition of the active material of the NiCd battery and thus, comparing the results of procedure A (250mg) with procedure B (100mg) we have that:

- For metals such as Cr and Pb there was no significant decrease in the intensity of the signals for the analytes studied, concluding that with the use of the acid mixture of procedure B (aqua regia) it proved to be more effective because we obtained the same signal intensity and used a smaller amount of active material for the analysis in question.

- For the Cd element, the results of the signal intensities obtained were expected, because by reducing the amount of active material for analysis, the proportion of signal intensity in procedure B decreases by half.
- For the element nickel, given the intensity of the signals obtained for procedure B, it was concluded that it was possible to digest a percentage of 34.3% lower than for procedure A. Concluding that the acid mixture used for procedure B was not possible to digest in the same amount as for procedure A, but the use of the acid mixture (aqua regia) is considered effective to be able to digest the nickel element in the sample in question.

It can be concluded that the acid mixture (aqua regia) has a high oxidizing power and is also very reactive, and to make it more efficient the mixture can be kept at rest before digestion.

The reason why the NiCd battery was chosen was due to the observation of the results of the EDS analyses, where high concentrations of the element cadmium were verified, which is an analyte of great importance in this study. Thus, procedure B proved to be more appropriate to promote the digestion of the samples.

The accuracy of the method using procedure B was also evaluated using the NiCd battery, where the ICP OES and FAAS techniques were used to compare the recovery results, the detection limits found were Cr 0.15 and 0.08 mgL-1, Cd 0.01 and 0.04 mgL-1, Ni 0.05 and 0.26 mgL-1; Pb 0.08 and 0.59 mgL-1

It is possible to verify that the method developed using the digestion procedure B (with the use of aqua regia) proved to be adequate for the analysis of Cr, Cd, Ni and Pb in battery samples. The recoveries obtained by ICP OES and FAAS ranged from 95-108% for all analytes and the ICP OES limits of quantification were the most appropriate for the samples in question.

The total concentration of analytes of interest present in the active material of batteries was determined using procedure B of digestion and analysis by ICP OES and the results obtained are presented in Table 4.

Table 4 - Total concentration of potentially toxic metals in the active material digested from batteries and cells by ICP OES with axial configuration.

Analytes (mg/kg)				
Elements	**Cr**	**CD**	**Nu**	**Pb**
Compose. Wave (nm)	205.56(II)	214.44(II)	232.00(I)	220.35(II)
Samples: BATTERIES				

Li-ion (A)	2.73 ± 0.17	21.94 ± 1.12	4.53 ± 0.12	2.01 ± 0.07
Li-ion(B)	2.44 ± 0.15	362.85 ± 11.19	15.69 ± 0.25	1.88 ± 0.09
Li-ion in. (A)	<LQ	266.67 ± 12.13	6.82 ± 0.11	4.03 ± 0.11
Li-ion in. (B)	0.94 ± 0.08	70.60 ± 1.05	14.29 ± 0.19	2.08 ± 0.03
NiCd (A,B,C)	0.96 ± 0.07	4561.58 ± 27.25	17.55 ± 0.92	1.91 ± 0.05
NiCd (A*, B*, C*)	1.19 ± 0.15	521.89 ± 17.42	475.06 ± 12.27 1089.67 ± 122.42 1250.69 ± 116.92	1.99 ± 0.06
Nimh	2.40 ± 0.12	47.26 ± 2.87	383.79 ± 16.44 773.58 ± 28.97	1.05 ± 0.02
BATTERIES				
Zn-C	0.90 ± 0.05	107.25 ± 5.48	108.45 ± 2.94	1.31 ± 0.10
Zn-C Heavy Duty	0.75 ± 0.06	8.04 ± 0.42	2.29 ± 0.09	1.93 ± 0.03
Li Button - ion (A)	*	43.15 ± 3.12	4.73 ± 0.08	4.79 ± 0.09
Li Button - ion (B)	1.69 ± 0.11	23.82 ± 1.59	3.75 ± 0.11	4.67 ± 0.05

Source: Author himself

As shown in Table 4, the total concentrations obtained for all analytes investigated were 5-15% higher than the values found in the leached extracts. The concentrations of Cd and Pb in the investigated samples are above the value established by the current legislation - CONAMA 401 of 2008, where the limits for cadmium is up to 0.002% and for Pb up to 0.1% by weight. Elements such as Cr and Ni are not controlled by legislation – CONAMA.

CONCLUSION

The characterization techniques (SEM, EDS and XRD) provided the obtaining of the particle size and the verification of the morphology of the active material. EDS did not present the sensitivity to analyze all potentially toxic metals in the investigated samples. It was also possible to identify by XRD the compounds constituting the active material of the samples.

Leaching tests using NBR 10.005/2004 proved to be an adequate procedure to promote the extraction of metals in the samples. For the batteries, 85-95% of the analytes were leached when compared to the values of total digestion. With the results obtained from the analysis of the leached extract by ICP OES and FAAS, it was possible to determine the concentration of metals that can be leached from the active material, and consequently, contaminate the environment. The concentrations obtained for Cd were above the limit concentrations established by NBR 10.004/2004, and, therefore, the samples were classified as hazardous waste. Other metals such as Cr and Pb were also found in the investigated samples, indicating that the presence of large amounts of this type of waste can cause leaching of these metals into the soil and contaminate the environment.

For the digestion of the NiCd battery sample, procedure B was the most appropriate to promote total digestion of the sample by microwave radiation, with the use of acid mixture (aqua regia) that provided a high oxidation power of the samples. The proposed procedure proved to be adequate, as the addition and recovery tests were 95-108%.

Among the procedures investigated and tested, the analytical procedure by digestion in an acidic medium assisted by microwave radiation, proved to be more efficient in the face of the acid mixture used. Additionally, the use of microwave radiation as an energy source for sample digestion allows a modern alternative to conventional procedures, thus reducing the time spent and the volume of reagents in the sample preparation stage.

Given the total concentrations obtained for all analytes investigated from the battery samples, a rate of 5-15% higher than the values found in the concentrations of leached extracts was found. The concentrations of Cd and Pb in the investigated samples are above the value established by the current legislation.

The chemical analyses carried out allowed the quantification of potentially toxic metals that are exposed to the environment, thus causing the contamination of soils and waters, in addition to putting human health at risk.

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