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Characterization of spent AA household alkaline batteries

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Abstract

The aim of this work is identification of the structural components of actual domestic spent alkaline AA batteries, as well as quantification of some of their characteristics. Weight, humidity, ash content, zinc and zinc oxide on anode, manganese on cathode and other metals, potassium hydroxide on the internal components and heating values for papers, anode and cathode were determined in several batteries. As expected, cathode, anode and the steel can container are the main contributors to the 23.5 g average weight of the batteries. Cathode is also the major contributor to the positive heating value of the batteries as well as to the heavy metals content. Mercury was detected in very low levels in these mercury-free batteries. Zinc and zinc oxide amounts in the anodes are highly variable. Results obtained were compared to information on alkaline batteries in the literature from 1993 to 1995; and a positive evolution in their manufacture is readily apparent. Data from the producer of batteries shows some small discrepancies relative to the results of this experimental work.
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1. Introduction

A battery is an electrochemical device that converts chemical energy contained in its active materials to electrical energy, providing a convenient source of portable energy with wide use in several consumer electronic products. The basic electrochemical unit, being referred to as a "cell", consists of an anode (negative electrode), a cathode (positive electrode) and an electrolyte (a liquid solution through which ions move). The electrochemical oxidation–reduction reaction during discharge involves the transfer of electrons from the anode that is oxidized, to the cathode that is reduced.

There are seven major types of household batteries as follows: alkaline zinc–manganese dioxide, zinc–carbon, mercury oxide, silver oxide, zinc–air, lithium and nickel–cadmium. This classification is based on the chemical nature of the active elements in the anode and cathode (Hurd et al., 1993). Alkaline zinc–manganese dioxide batteries, commonly referred to as alkaline batteries, account for the major market share of household batteries in Portugal and even in the entire world (Hurd et al., 1993). The most popular format is the AA standard, a cylindrical format with a diameter between 13.5 and 14.5 mm, a height between 49.0 and 50.5 mm and a weight of approximately 23 g.

Alkaline batteries use powdered zinc as the negative electrode (anode), manganese dioxide (MnO_2) with graphite as the positive electrode (the cathode), and highly conductive potassium hydroxide (KOH) as the electrolyte (Hurd et al., 1993). These batteries use a form of manganese dioxide known as "battery grade" or electrolytic manganese dioxide (EMD) instead of either chemical MnO_2 or natural ore, because of its higher manganese content, increased reactivity and greater purity. The composition of the typical cathode is reported as containing 79–85% MnO_2, 7–10% graphite, 7–10% aqueous KOH and 0–1% binding agent. The KOH elec-

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trolyte is concentrated in the range of 35–52%, which affords greater conductivity and a reduced hydrogen-gassing rate. Powdered zinc is used for the anode to provide a large surface area for high-rate capability and to distribute solid and liquid phases more homogeneously. The composition of a typical anode includes 55–70% powder zinc and 25–35% aqueous KOH (Linden, 1995). In addition, alkaline batteries may contain metals, plastic and paper components.

On discharge, the manganese dioxide cathode undergoes a reduction to MnOOH, and further, at a lower voltage, MnOOH is discharged to Mn_3O_4. The anode discharge reaction in highly caustic electrolyte produces $Zn(OH)_2$ that slowly dehydrates to ZnO. Reaction (1) is considered the overall reaction on these cells (Linden, 1995).

$$3MnO_2 + 2Zn = Mn_3O_4 + 2ZnO \quad (1)$$

In terms of construction, a cylindrical steel can is the container for the cell that also serves as the cathode current collector. The cathode is positioned inside the can in the form of a hollow cylinder in close contact with the can's inner surface. Inside the hollow center of the cathode are placed layers of separating material. Inside of that is the anode, with a metal collector contacting it, and making connection through a plastic seal to the negative terminal of the cell. The cell has top and bottom covers and a plastic jacket (Hurd et al., 1993).

Knowledge of the structure and composition of spent batteries is an important step for evaluating the environmental impact of the alternatives to deal with this type of waste, usually incineration or landfilling, since those characteristics determine the quality, quantity and timeframe for release of emissions. For example, in the case of landfilling, where emissions result from the degradation of the batteries, metals released from the inner parts of them strongly depend on degradation of the outer parts, and not only on the overall composition. Gaseous emissions from incineration not only depend on the overall chemical composition of the batteries but also on the form of the elements whether in elemental state or as compounds.

Data on the characteristics of alkaline batteries produced in the past is found in some references, but there is the risk of not matching the characteristics of present batteries (Linden, 1995; Hurd et al., 1993). Consequently, this study included a structural analysis and established the actual composition of spent AA alkaline batteries, the household batteries widely used in Portugal. This provides an actual source of information for the characterization of this waste stream and better interpretation of the results from the work carried out with the objective of assessing the environmental impact of batteries on landfilling and incineration.

2. Experimental

The laboratory work developed for characterizing the target batteries included the following steps: sampling the spent batteries; identifying the structural components; weighing the separated components; determining the moisture content; determining the ash content; analyzing zinc in the anode as metal as well as zinc oxide; quantifying for carbon in the cathode; analyzing for manganese in the cathode; determining the concentration of heavy metals in the components such as Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Si, Tl, V, Zn, Hg and As; analyzing for potassium hydroxide in the internal components; determining sulfates in the cathode and in the anode; measuring chlorides in the cathode and in the anode; and determining the higher heating value for paper, the anode and the cathode.

The most important aspects of the methodology followed in each determination are presented below.

2.1. Sampling

The spent alkaline batteries made by Duracell®, format AA, with expiration date of March 2003, were obtained in a central collection site in the city of Porto. The batteries were stored at the collection site in a drum with different types of household batteries deposited by residents. Some of the batteries originated from street collection containers distributed throughout the city as well as from collection points located in commercial areas.

2.2. Identification of structural components

To determine the structural components, batteries were opened at the laboratory and components that could be physically separated were located (according to references) and taken apart (Hurd et al., 1993), as shown in Fig. 1. The main base material of the plastic grommet, separators, and plastic sleeve were identified using laboratory tests. Magnetic properties were used to distinguish between ferrous and non-ferrous metals in the components. Visual observation was used to identify materials made out of cardboard.

Laboratory techniques based on solubility properties of polymers in different solvents and Infrared Spectroscopy with direct reading of transmittance on a wavelength range from 400 to 4000 wave lengths were used for the identification of polymer and separators (American Society for Testing and Materials, 1992). Spectra obtained for these materials were compared with spectra from known materials.

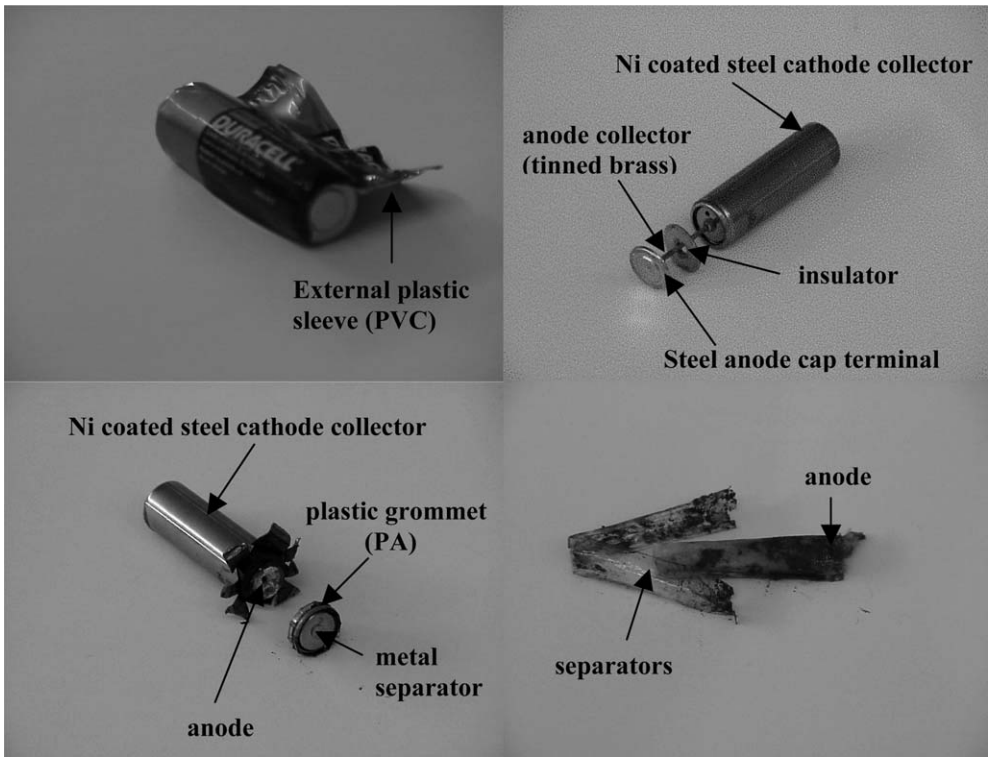


Fig. 1. Separating AA spent alkaline batteries components in laboratory.

2.3. Weight of components

Five of these batteries were dismantled and all of their components (except the anode and the cathode) were slightly washed with distilled water. After washing, the items were dried at 105 °C for 30 min, then cooled to room temperature in the dessicator and weighed. This procedure of drying, cooling and weighing was repeated several times with all of the components. In the case of hygroscopic components, such as the anode and the cathode, the weight considered for a certain battery was the minimum value obtained in all of the drying and cooling cycles. For all of the other components, the weight considered was the average of the two last values whose difference was less than 0.5 mg. This criterion was adopted as the constant weight definition. Table 1 presents the average results obtained for five batteries.

2.4. Moisture content

This parameter was determined for all of the components from two batteries, except for the cathode and the anode, whose determination was based on a sample of ten batteries. The difference in weight before and after drying at 105 °C until a constant weight was reached was taken as the moisture content in the component. The moisture content, expressed as a percentage of the wet weight of each component, was taken as the average value of the corresponding wet and dry weight differences. In the case of the anode, due to the high scatter of values of moisture contents, the results are presented as the corresponding range.

2.5. Ash content

The ash content was determined in all the components of two batteries, except for the metal components, as well as on the entire cross-cut batteries. The components were dried at 105 °C until constant weight was reached and then ashed at 1000 °C for 1 h. Ash was calculated as the residue weight after cooling.

2.6. Zinc on anode as metal and as zinc oxide

Since zinc is on the anode as metal and as zinc oxide, both these forms were quantified after drying the anode at 105 °C until constant weight was reached. Zinc oxide was dissolved by leaching the anode with a stirred Muspratt solution (5 g NH_4Cl, 20 ml NH_4OH conc. and 50 ml distilled water) for 1 h at room temperature. The solution was filtered. Zinc dissolved on the filtered solution was determined by Atomic Absorption Spectrometry (AAS) and counted as zinc oxide. The solids retained on the filter were reacted with a heated solution containing 2 g of $CuSO_4$ in 50 ml of distilled water for 1 h. The amount of zinc in that solution was also determined by AAS and counted as metallic zinc in the anode. These determinations were made with the anodes from four batteries.

Table 1
Physical characteristics of spent AA alkaline batteries

Components	Base material	Average dry weight[b] (g per battery)	Moisture content[b] (%, dry basis)	Ash content[b] (%, dry basis)	Higher heating value[b] (kJ kg^{-1}, dry basis)	Lower heating value (kJ kg^{-1}, dry basis)
Anode cap	Steel	0.288 ± 0.003	–	–	–	–
Insulator	Cardboard	0.060 ± 0.002	6.4 ± 0.1	9.3 ± 0.5	$23.8 \times 10^{3} \pm 0.4 \times 10^{3}$	22,675
Plastic grommet	Polyamide (PA)	0.215 ± 0.005	1.4 ± 0.2	1.0 ± 0.3	$35 \times 10^{3} \pm 2 \times 10^{3}$	33,041
Metal separator	Steel	0.377 ± 0.005	–	–	–	–
Anode collector	Tin-plated brass	0.438 ± 0.004	–	–	–	–
Anode	Zn + ZnO + KOH	3.86 ± 0.05	1.8–28.7	99 ± 1	$6.1 \times 10^{3} \pm 0.7 \times 10^{3}$	6142
Separator	Paper	0.107 ± 0.009	5 ± 1	2.4 ± 0.2	$26 \times 10^{3} \pm 2 \times 10^{3}$	25,008
	Cellophane	0.045 ± 0.003	10 ± 1	5.26 ± 0.06	$22.09 \times 10^{3} \pm 0.7 \times 10^{3}$	20,857
Cathode	MnO_2 + C + KOH	11.9 ± 0.9	8 ± 2	88.3 ± 0.4	$6.8 \times 10^{3} \pm 0.8 \times 10^{3}$	6799
Cathode collector	Steel	4.01 ± 0.05	–	–	–	–
Plastic sleeve	Polyvinylchloride (PVC)	0.23 ± 0.01	1.7 ± 0.2	5.28 ± 0.08	$20.4 \times 10^{3} \pm 0.9 \times 10^{3}$	19,455
Entire batteries	–	23.5[a] ± 0.4	–	98.1 ± 0.2	–	–

–, not determined.
[a] As collected.
[b] 95% confidence interval.

2.7. Carbon in the cathode

The cathode was ground, then washed with hot distilled water and neutralized with concentrated HCl for the removal of KOH. The residue was dried at 105 °C until constant weight was reached, then combusted at 1000 °C for 30 min in a tubular oven with an oxygen flow of 0.42 L min^{-1}. Carbon dioxide released during combustion was absorbed in 50 ml of a 50% (w/v) KOH solution. The weight difference of the solution before and after bubbling the off-gases of combustion was taken as the CO_2 produced; therefore, it was used to estimate the carbon content of the cathode. This determination was repeated with cathodes from five batteries.

2.8. Manganese in cathode

The cathode was digested with an aqueous solution of HCl (1:1) and H_2SO_4 (conc.), followed by manganese reduction to Mn^{2+} with Na_2SO_3 and its determination by potentiometric titration with permanganate in a neutral pyrophosphate solution according to a standard method (Bassett et al., 1981). This determination was made on three batteries.

2.9. Concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb, Sb, Si, Tl, V, Zn, Hg and As in components

The heavy metals analyzed for each component were selected taking into consideration the nature of the component as well as the information obtained in the literature. The methods of digestion were adapted to the components according to the target metals and its base material (United States Environmental Protection Agency, 1982, Method 3050B and Method 3052). For mercury determination, the samples were digested with a sulfuric–nitric acid mixture in a water bath at 60 °C according to a method of the English Department of the Environment. For the determination of silicium in the cathode steel collector, all sample dissolution was guaranteed. After digestion, all metals were quantified in the solution by AAS using the technique and the method proposed by standard methods (United States Environmental Protection Agency, 1982), excepting for manganese in the cathode. Manganese in the cathode was determined as previously described. Table 3 shows the digestion methods and AAS techniques used for each component and metal. Metals were determined in the components obtained from a sample of batteries, as follows:

Table 2
Chemical composition of cathode, anode and KOH content of internal components

Components	C[a] (g C per 100 g of dry cathode)	Mn[a] (g Mn per 100 g of dry cathode)	Metallic Zn (g Zn per 100 g of dry anode)	Zn as ZnO (g Zn per 100 g of dry anode)	KOH[a] (g per battery)	Sulfates[a] (%, dry basis)	Chlorides[a] (%, dry basis)
Cathode	6 ± 1	45 ± 4	–	–	–	0.37 ± 0.04	0.0010 ± 0.0003
Anode	–	–	0.71–62.9	1.5–35.8	–	0.010 ± 0.002	0.007 ± 0.002
Cathode + anode + separators	–	–	–	–	0.9 ± 0.2	–	–

–, Not determined.
[a] 95% confidence interval.

Table 3
Digestion methods and AAS techniques used for each component

Components	Metals quantified	AAS technique	Digestion method
Anode and cathode	Sb, Cd, Cr, Co, Cu, Pb, Ni, Tl, V, Zn and Mn on anode	Direct aspiration (Methods 7040, 7130, 7190, 7200, 7210, 7420, 7520, 7840, 7910, 7950, 7460, respectively)	Digestion with nitric acid and hydrogen peroxide solution at 95 °C (Method 3050B)
	As	Gaseous hydride (Method 7061A)	
	Hg	Cold vapor technique (Method 7470A)	Digestion in a solution of sulfuric and nitric acids at 60 °C Oxidation with permanganate
Plastic sleeve	Sb, Cd, Cr, Co, Cu, Pb,Mn, Ni, Tl, V, Zn	Direct aspiration (Method 7040, 7130, 7190, 7200, 7210, 7420, 7460, 7520, 7840, 7910, 7950, respectively)	High pressure oxidation with hydrogen peroxide solution (Method 3052) Calcination of residue at 500 °C
	As	Gaseous hydride (Method 7061A)	Digestion of ash and solution from oxidation with concentrated nitric acid
Other components	Sb, Cd, Cr, Co, Cu, Pb, Mn, Ni, Tl, V, Zn	Direct aspiration (Method 7040, 7130, 7190, 7200, 7210, 7420, 7460, 7520, 7840, 7910, 7950, respectively)	Digestion with nitric acid and hydrogen peroxide solution at 95 °C (Method 3050B)
	As	Gaseous hydride (Method 7061A)	
	Si (only on cathode collector)	Direct aspiration	Internal method (Almeida and Pinho, 2001)

- cathode, a sample of three batteries was used for all metals, except for mercury and silicium where a sample of four batteries was used;
- anode, same as the cathode except for silicium that was not quantified;
- other components, a sample of four batteries was used for all metals although mercury and silicium were not quantified.

Table 4 shows the limits of the ranges found.

2.10. Potassium hydroxide in the internal components

The anode, the cathode, and the paper and cellophane separators were ground and dried at 105 °C until constant weight was reached. Potassium hydroxide in each of these components was removed by washing them with hot distilled water. Potassium in the solutions was determined using a gravimetric standard method that comprises the precipitation of K in the form of sodium and dipotassium hexanitrocobaltate (III), by adding a sodium hexanitrocobaltate (III) solution in nitric acid (Bassett et al., 1981). The precipitate was dried at 105 °C for 2 h and then weighed. This determination was made with components from two batteries.

2.11. Sulfates in the anode and in the cathode

The anode and the cathode were washed separately with hot distilled water. Sulfates were determined in the wash water using a gravimetric method (American Public Health Association, 1992). This determination was performed for five batteries.

2.12. Chlorides in the anode and in the cathode

The anode and the cathode were washed separately with hot distilled water. Chlorides were determined in the wash water using the Volhard method (Bassett et al., 1981). This determination was conducted for five batteries.

2.13. Higher and lower heating value determination

The heating value (Moran and Tsatsaronis, 2000) of a residue is an important parameter for the analysis of its behavior during an incineration process.

The higher heating value of all battery components, except the metallic ones, was determined using a Parr oxygen bomb calorimeter where a known amount of sample is ignited in an enclosed atmosphere of pure oxygen by short-circuiting an electric wire (Brunner, 1994).

Table 4
Concentration of heavy metals in battery components (mg g^{-1} of dry component, except for Hg and As, expressed as μg g^{-1})

Metals components	As	Cd	Co	Cr	Cu	Hg	Mn	Ni	Pb	Sb	Si	Tl	V	Zn	Total (mg per battery)
Anode cap	4.7	<0.011	0.11	0.96	0.10	–	2.1	14.3	0.16	<DL	–	<DL	<DL	0.009	5.5
	6.3	0.017	0.12	1.1	0.47		2.3	16.4	0.18					0.20	
Insulator	<DL	<DL	<DL	<0.082	<DL	–	<0.050	<0.11	0.22	<DL	–	<DL	<DL	<0.022	0.065
				0.11			0.092	1.4	0.44					0.40	
Plastic grommet	<DL	<DL	<DL	0.028	<DL	–	<0.013	<0.029	0.079	<DL	–	<DL	<DL	0.051	0.19
				0.035			0.38	0.086	0.096					1.1	
Metal separator	3.7		0.087	2.4	0.072	–	2.2	0.19	0.15	<DL	–	<DL	<DL	0.005	2.1
	7.1	0.012	0.12	2.6	0.14		2.5	0.23	0.17					0.045	
Anode collector	<DL	<DL	<DL	<0.012	589	–	<DL	<0.015	0.046	<DL	–	<DL	<DL	317	428
				0.022	692			0.048	0.069					365	
Anode	<0.033	<DL	<DL	<DL	<DL	<DL	0.011	<DL	0.042	<DL	–	<DL	<DL	792	3154
	0.11						0.025		0.049					830	
Separator paper	<DL	<DL	<DL	<0.05 3	<DL	–	0.73	<DL	0.14	<DL	–	<DL	<DL	13.6	2.4
				0.30			2.87		0.63					38.8	
Cellophane	<DL	<DL	<DL	<0.14	<DL	–	0.16	<DL	<0.26	<DL	–	<DL	<DL	13.8	2.0
				0.44			0.57		0.83					58.0	
Cathode	0.065	<DL	0.027	0.007	<DL	<0.11	453[a]	0.018	<0.011	<DL	–	0.084	<DL	9.0	5487
	0.11		0.029	0.008		0.43		0.030	0.052			0.097		10.1	
Cathode collector	2.8	0.010	0.099	2.0	0.065	–	2.0	13.9	0.087	0.095	<0.096	0.076	<DL	0.034	80
	5.0	0.015	0.12	2.1	0.097		2.3	16.2	0.094	0.12	0.41	0.093		0.075	
Plastic sleeve	<DL	<DL	<DL	<0.050	<0.043	–	<0.030	0.070	<0.10	<DL	–	<DL	<DL	<0.013	0.19
				0.40	0.060		0.10	0.18	0.12					0.47	
Battery total amount (mg per battery)	0.021	0.060	0.84	9.5	281	0.0038	5383	65	1.2	0.44	0.84	1.4	0.0	3418	9163

<DL, below detection limit.
–, not determined.
[a] Determined by potentiometric titration.

Each of the components was first ground, dried at 105 °C until constant weight was achieved, and then mixed with benzoic acid to guarantee complete combustion of the mixture. The results obtained were corrected for the use of benzoic acid, according to the equipment instructions, and are expressed on a dry basis.

The lower heating values were calculated using information from the literature (Sundqvist, 1999).

The hydrogen content of each component on a dry basis ($X_{H,dry}$) needed for the calculations, was estimated using the hydrogen content of the combustible (organic) fraction of each component ($X_{H,c}$) and its ash content on a dry basis ($X_{ash,dry}$), as follows:

$$X_{H,dry} = X_{H,c}(1 - X_{ash,dry}), \quad (2)$$

where $X_{H,c}$ means the hydrogen content in the combustible (organic) fraction of the product (kg kg^{-1}) and $X_{ash,dry}$ the ash content in the product (kg kg^{-1}, dry basis).

The value used for the ash of each component was that given in Table 1. The hydrogen content in the combustible fraction of the components was estimated as follows: (i) for both the anode and the cathode it is nil, since they contain only inorganic compounds; (ii) for the cardboard insulator as well as paper and cellophane separators it was based on tabulated values

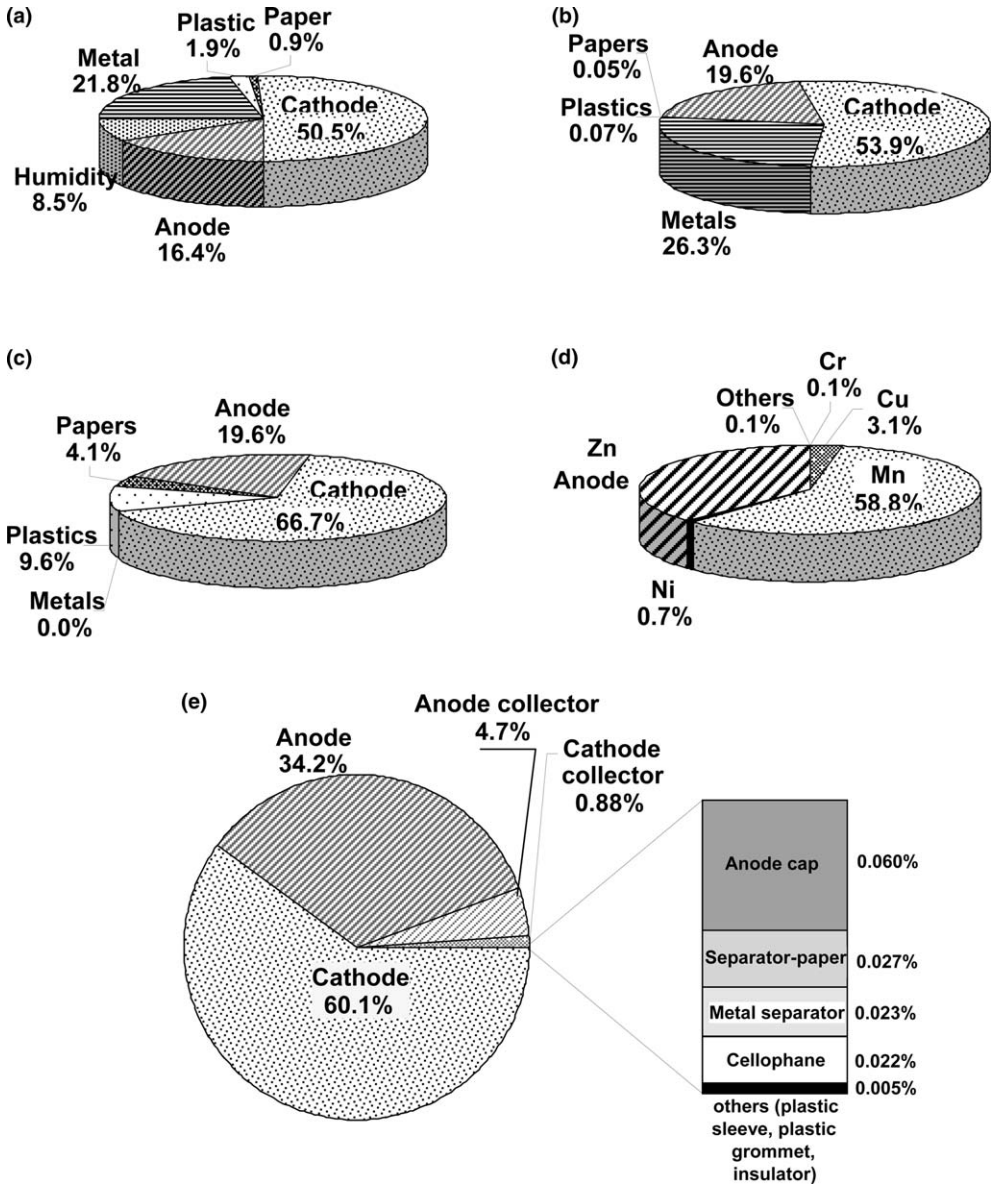


Fig. 2. Characteristics of spent AA alkaline batteries: (a) components and materials; (b) contribution of components to ashes; (c) components contribution to lower heating value; (d) metals content, except iron. Others includes As, Cd, Co, Hg, Pb, Sb, Si, Tl and V; (e) Heavy metals in components.

from the literature derived from the typical data on their ultimate analysis (Tchobanoglous et al., 1993); and (iii) in the case of the plastic components made either with PVC or PA, the hydrogen content in the combustible fraction was determined according to the chemical formulae of these polymers. The hydrogen content in the combustible (organic) fraction of each component, $X_{H,c}$ (kg kg^{-1}), is 0.062 for the insulator, 0.064 for the separator, 0.097 for the plastic grommet and 0.048 for the plastic sleeve.

3. Results and discussion

The average battery weight, calculated using a sample of 14 batteries, was 23.5 g. The components identified and listed in Table 1 with the indication of the base material, its average dry weight and moisture content show that the dry cathode and anode account for 50.5% and 16.4% of the total weight of the battery, respectively. Metal components, plastics and paper represent respectively 21.8%, 1.9% and 0.9% of the weight as depicted in Fig. 2(a). Metal components are comprised of about 91.4% steel and 8.6% tin-plated brass. Plastic components include 48.0% PA and 52.0% PVC; and paper-based components are comprised of, respectively, 28.3% cardboard, 50.5% paper and 21.2% cellophane. Moisture content of the batteries (estimated through the average weight of the batteries as collected and on the average total dry weight of all the components) is around 2 g, which represents 8.5% of the total mass. Also, the moisture content of the anode varies from 1.8% to 28.7% as seen in Table 1.

The total amount of ash from all non-metallic components is 14.3 g per battery. If it is considered that non-powdered metallic components are 100% ash, the total amount of ash is 19.4 g per battery. However, when determined directly on the cross-cut batteries, the total amount of ash is 21.1 g per battery, around 98.1% of its dry weight. These differences reflect the level of materials oxidation that is achieved when batteries are loaded into the furnace either as highly damaged or practically intact; when batteries are practically intact the level of release of the inner parts is more restricted thus increasing the amount of ash. Fig. 2(b) summarizes the individual contribution of each component to the battery ash and assumes 100% ash for the non-powdered metallic components. As shown, the cathode is the main contributor to ash formation with an estimated value of 53.9%, followed by the metallic components with 26.3% and the anode with 19.6% of the total.

Zinc metal in the anode varies from 0.71% to 62.9% and ZnO from 1.5% to 35.8% of the total dry mass, showing an enormous variability. The distribution of zinc between metal and zinc oxide depends on the battery manufacturer, but also on its usage conditions, namely the discharge rate which may vary widely.

Carbon is 6.0% of the cathode's dry mass. Since manganese in the cathode of new batteries is present as MnO_2, the 45.3% Mn value indicated in Table 2 corresponds to an initial amount of 71.7% MnO_2.

Potassium hydroxide in the anode, the cathode and the separators accounts for 4.3% of the total mass of the battery on a dry basis which corresponds to the 0.92 g as shown in Table 2. Sulfates and chlorides are also present in the anode and in the cathode in the approximate amounts of 43 and 0.4 mg for sulfates and 0.12 and 0.27 mg for chlorides, respectively.

The higher heating values of non-metal components presented in Table 1 show plastic grommet and paper materials as the components with the highest heating values in AA batteries. Fig. 2(c) presents the contribution of each component to the total lower heating value of the battery estimated as explained before. According to these results, the cathode is the main contributor to the energy released by batteries on combustion and it accounts for 66.7% of the total heat generated in the process. The anode is the second contributor to the exothermic behavior of the batteries. This effect is due to the highly exothermic oxidation reaction of $Zn \rightarrow ZnO$ that amounts to about 5335 J g^{-1} of zinc (Perry and Green, 1997).

Fig. 2(d) shows the main metals in batteries expressed as a percentage of the mass of all metals determined. These percentages were calculated using the average values of the determinations carried out and are shown in Table 4. Manganese and zinc account for 58.8% and 37.3% of the metals present in batteries, respectively. Copper, nickel and chromium have still reasonable percentages, but all other metals evaluated, i.e., As, Cd, Co, Hg, Pb, Sb, Si, Tl and V, are found in trace amounts.

The contribution of the different components to the overall amount of each one of the heavy metals is presented in Fig. 3. As shown, the cathode collector contributes substantially to the concentration of As, Cd, Co, Cr and Ni, whereas the anode collector is the main contributor to the concentration of Cu, since it is responsible for 99.8% of its total amount. As expected, the cathode and the anode contribute the most manganese and zinc, respectively 99.8% and 92.0% of its total. Cathode and anode collectors contribute 33.1% and 30.5% lead, and 76.4% and 23.6% thallium, respectively, although both total amounts of these metals are very small. Fig. 2(e) shows the contribution of each component to the total amount of heavy metals. The anode and the cathode have the higher contribution with 34.2% and 60.1% of the total, respectively.

These data are compared with data published in the literature (Hurd et al., 1993;Linden, 1995), according to Table 5, for both new and post-consumer batteries. The mass percentage of the anode in actual batteries

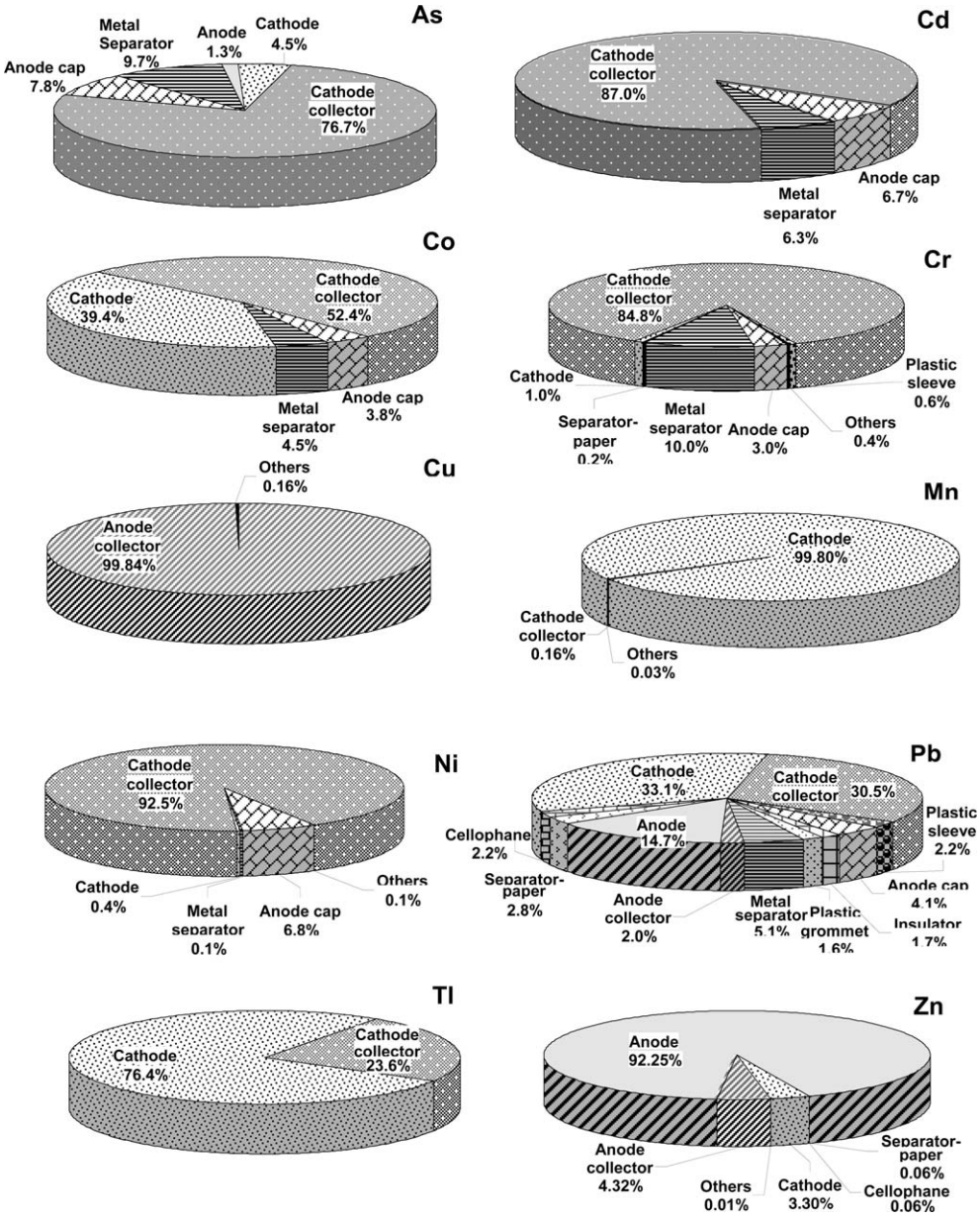


Fig. 3. Contribution of components for the AA spent alkaline batteries content in some metals.

shown in the 4th column was obtained by subtraction due to the variability found in the determinations for moisture content.

The present data is closer to that given for past post-consumer batteries than for new batteries. The only exceptions are metal and anode contents whose values are closer to those given for past new batteries. For post-consumer batteries, almost all of the components' values differ significantly from our data. The cathode and the anode have higher relative mass in actual batteries in contrast with the other secondary components that contain and support those active elements. Only the anode collector has a similar percentage. Therefore, we can conclude that a great change took place in the composition of these batteries over the years. The values reported in 1993 for the percentage of metals differ greatly for new and post-consumer batteries. These are smaller for Cu, Mn and Zn and higher for Fe and Hg in post-consumer batteries. Compared to our data, the actual percentages of heavy metals are significantly smaller with special emphasis on mercury, as expected. The percentages of Cu, Mn and Zn in actual post-consumer batteries are close to those given in 1993 for new batteries.

The typical composition of the cathode in 1995 (Linden, 1995) was 79–85% MnO_2, 7–10% graphite, 7–10% KOH (aqueous 35–52%) and 0–1% of optional binding agent, indicating for MnO_2 and C values

Table 5
Comparison of the results of this work with data from the literature (Hurd et al., 1993; Linden, 1995)

Material/component (%)	Data from the literature		Present work
	New	Post-consumer	Post-consumer
Plastic	4.09	3.29	1.94
Metal	28.74	37.27	19.9
Paper	5.02	4.6	0.96
Brass (anode collector)	1.96	1.99	1.86
Cathode	37.61	39.23	54.66
Anode	22.58	13.62	20.69[a]
Element (%)			
As	0.0002	0.0005	0.000089
Cd			0.00026
Co			0.0036
Cr	0.098	0.1335	0.040
Cu	1.38	0.0071	1.2
Fe	16.92	32.73	
Hg	0.012	0.483	0.000016
In	<0.0009	<0.0009	
K	4.17	2.56	2.73[b]
Mn	22.82	2.88	22.9
Ni	0.3695	0.4323	0.28
Pb	0.0085	0.004	0.0051
Sb			0.0019
Si			0.0036
Sn	<0.0011	0.0171	
Tl			0.0060
V			<LD
Zn	17.25	9.69	14.5

[a] Obtained by balance.
[b] In anode, cathode and separators.

higher than those now obtained. The presence of sulfates, Na and Fe, among others, in the manganese dioxide used in alkaline batteries was also comparable to the sulfates content above the value now obtained. For the anode, the 1995 composition was 55–70% zinc powder, 25–35% KOH (aqueous 35–52%), 0.4–2% gelling agent, 0–2% ZnO, 0–0.05% inhibitor and 0–4% mercury. Some impurities, namely Cd, Fe, Ag and Cu, were listed for zinc powder. Compared to the actual composition, the zinc content is substantially higher and purer, since it is around 81% of the anode with no traces of cadmium and copper. Mercury in the actual mercury-free batteries is also at non-detectable levels in the anode.

More recent data about the composition of alkaline batteries (Watson, 1999) also show some discrepancies with our data. There is a significant difference of about 52% in the tin-plated brass; we obtained 0.44 g compared to 0.29 g/battery from the producer data. Other differences observed in structural components include nickel, KOH, steel can, carbon in the cathode and PVC whose values are 45.8%, 27.0%, 18.4%, 17.9%, respectively, lower than those reported. Producer data does not refer to the PA base material of the plastic grommet or to the Pb, Cd and Hg, which were detected at low levels of 1.2, 0.06 and 0.004 mg/battery in this work. Other metals, such as Cu and Cr were not referred to by the reported data. Zinc and manganese are only 8.6% less and 3.0% more than the values reported by the producer. Most of these differences may be attributed to the natural variability in methodologies for sampling and chemical analyses. Some other discrepancies could be related to manufacturer improvements with respect to both environmental and technical performance. For example, as one of the manufacturing tendencies is lightweighting batteries, it is not unusual that a 19.5% lower weight was found for the steel can in the more recent batteries used in this work.

Despite all of this progress, the data confirms that spent batteries are a highly alkaline waste with several metals in metallic form as well as in metal compounds. Some of them are expected to be partially released during the disposal or treatment option used for this waste stream, usually either landfilling or incineration.

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