JASEM ISSN 1119-8362

Full-text Available Online at www.bioline.org.br/ja
J. Appl. Sci. Environ. Mgt. *September,* 2006
Vol. 10 (3) 37 - 41

Determination of Lead and Cadmium Contents of Dry Cell Batteries Available in Nigeria

[1]*NNOROM I.C, [2]OSIBANJO O

[1,] *Department of Industrial Chemistry, Abia State University, P. M. B 2000, Uturu, Abia State, Nigeria.*
[2]*Department of Chemistry, University of Ibadan, Ibadan, Oyo State, Nigeria*

ABSTRACT: Lead and cadmium content of different brands and sizes (N=38) of dry cell batteries (zinc-carbon Leclanche systems) available in Nigeria were determined by atomic absorption spectrometry after acid digestion. The average Pb and Cd content of the dry cells are 1077.9±751.7mg/kg (Range 42-3170mg/kg) and 108.3±81.4mg/kg (Range 4.6-410mg/kg) respectively. The mean Pb and Cd contents of dry cells with metal outer cover were significantly lower ($p < 0.005$) than the corresponding values for dry cells with non-metallic cover. The highest Pb and Cd values were observed in dry cell batteries imported from China. Higher mean Pb and Cd value were observed in dry cells from China (1368.36 vs. 151.47mg/kg), compared to values for dry cells from Indonesia (1032 vs. 84.4mg/kg),Japan (715.2 vs. 131.48mg/kg) and Korea (1137.5 vs. 81.45). Lower Pb and Cd values were obtained in dry cells from Malaysia (709 vs. 12.5mg/kg), Spain (702 vs. 65.8mg/kg), United States (303 vs. 11.1mg/kg) and in the only surviving local brand (408 vs. 34.5mg/kg).Our study revealed that there is an urgent need to introduce an adequate well-established system for collection, separation, storage and management of municipal and industrial wastes containing primary and secondary battery wastes and similar toxic materials to halt the open burning of such wastes within inhabited areas. There is an urgent need to develop in Nigeria an appropriate technology following the principles of waste minimization and sustainable development. @JASEM

The management of primary and secondary battery wastes is essential in order to avoid or minimize inappropriate disposal which may result in harm to the environment and the human health. Household batteries contribute 52% of Cd and 88% of Hg found in the municipal solid waste, yet they comprise less than 1% by weight of municipal solid waste (Shapek, 1996).The toxicity and widespread pollution by lead is well known. In fact, lead has been described as the most severe environmental contaminant to arise in human civilization (Smith and Flegal, 1995). Although Pb is ubiquitous in the environment Pb as a pollutant is essentially of anthropogenic origin. The polluting nature of the manufacturing processes of both primary and secondary batteries to the environment (Ward et al*.,* 1977; Semu et al., 1986; Onianwa and Fakayode, 2000) and the adverse health effect on battery industry employees and their families have been established (Bader et al, 1999; Ritcher et al, 1979; Fergusson et al, 1981; Oleru et al, 1983). The absence of environmental protection equipment near battery and waste battery recycling facilities has been associated with increase of Pb in human tissue samples (Wohl et al, 1996; Bader et al, 1999). The manufacture of dry cell batteries expose employees to Pb, Mn, Zn, Cd and suspended carbon black dusts which usually contains polyaromatic hydrocarbons (PAHs). Exposure to carbon black dust in dry cell battery facilities results in significant loss in pulmonary function (Oleru et al, 1983). Higher levels of Pb and Mn have been observed in the body tissues of primary and secondary battery employees and their family members (Bader et al, 1999; Wohl et al, 1996; Lai et al, 1997). The high levels of especially Pb observed in the tissue samples of the employees family members reveals a problem arising from employees' transferring lead dust home, probably in their working cloths (Fergusson et al, 1981).

Dry cells are non-rechargeable and of single use. They constitute household hazardous waste when 'dead', that is when the components have reached their equilibrium concentrations. The open burning of wastes containing municipal and industrial wastes results in the emission of heavy metals into the atmosphere with fly ash and after fallout, metals in dusts and soils. This form of metal pollution have been classified as an environmental transfer of metal and not a true source of metallic pollutant (Ayres and Ayres, 1994).This is because the metals emitted must have been originally embodied in items of consumption discharged as waste. These toxic metals can be leached from ash and cinder into domestic surface waters by acidic wet precipitation which may result from the large-scale gas flaring by the Nigerian petroleum and natural gas sector. This leaching process can be enhanced by charges in pH, redox potential and the presence of organic chelators. Highly acidic pH of 3.4 has been observed in some natural surface waters in industrial areas of Nigeria (Sridhar and Bammeke, 1986). Such acidic pH can enhance the mobility of metals. The major streams in the industrial cities of Nigeria are already seriously polluted by industrial waste (Ajayi and Osibanjo, 1981) and pesticide residues (Nwankwoala and Osibanjo, 1992). The aim of the present study was to determine the Pb and Cd contents of dry cell batteries available in Nigeria in order to assess the contribution of such consumptions to environmental heavy metals pollution in Nigeria.

Correspondence: Email: chidiabsu@yahoo.co.uk Phone: +234-803-792-845-2

Table 1. Sizes and brands of dry cells used in the study

Size D (R20)	Crepower,Rapid,Maexcell,HiWatt(HD),ABC, Diamon, Energy,Swan,Supower,HiWatt Three Circle,Lonlife,Berec,Simba,Flash, Tigerhead, Solar Energy, Getready,
Size C (R14C)	Champion
Size AA (R6P)	Royal, New Topcell, Rocket, Motoma, Tim, HWMAX, Sony Super, Tunar (High Tech), Golden Bell, GLIP2000, Panasonic, Yarico, Tunar (Larga Duracion), Tudor Larga Duracion), Domex, Ducelar, Paideer, Konnoc
Size AAA (RO3)	Xiongjian, Bravepower

MATERIALS AND METHOD

Dry cells of different brands and sizes were purchased from retail outlets in Okigwe, and Umuahia in Southeastern Nigeria. The dry cells were mainly of the Zn/MnO_2 system. The brands of dry cells used in this study is shown in Table 1.The dry cells were carefully opened and dried to constant weight for 12 hours at 110^0C in an oven. The carbon rod and cathode mix (MnO_2 + carbon + electrolyte) were ground in a porcelain mortar into a fine particle 'black mix'. To obtain a representative sample of the dry cell as is discarded, a weight ratio of 2:3 was used for the metal cover and the black mix respectively. 0.5g of the sample was digested with 2:1 mixture of HNO_3/$HClO_4$. After the initial violent reaction with evolution of brown fumes had subsided (ca.10min), the digestion flask was covered with a watchglass and digested up to 150^0C in a regulated programmable aluminum digestion block. This was then treated with two portions of the HNO_3/$HClO_4$ and evaporated to near dryness. More acid mixture was added and the digestion continued until dense white fumes was evolved, marking the completion of the digestion process. This was then evaporated to near dryness and taken up in 1M HNO_3 filtered through pre-acid washed Whatman No. 4 filter paper into a 10ml volumetric flask and made up to mark with the 1M HNO_3. This was subsequently analyzed for Pb and Cd using flame atomic absorption spectrophotometer (Buck Scientific, Model 210). Internal quality control procedure with re-tests of standards was undertaken. A recovery study of the total analytical procedure was carried out by spiking portions of two previously analyzed brands with varying concentrations of Pb and Cd. These were homogenized, redried and passed through the digestion and analytical steps. Results reported are averages to of duplicates.

Table 2. Lead and cadmium contents (Mean ± SD) of some dry cell batteries vailable in Nigeria according to size (µg/g dry weight).

Battery size	Lead	Cadmium
Size D (R20)	988.78± 826.26 (616.83)* 42 – 2670 **	105.26 ± 91.08 (67.89) 8.1 – 410
Size C (R14C)	1748	141.80
Size AA (R6)	1146.33 ± 712.48 (952.98) 154– 3170	93.30 ± 59.95 (67.54) 9.5 – 320
Size AAA (R03)	929 ± 1039.45 (568.17) 194 – 1664	253.6 ± 93.9 (244.75) 187.2 – 320

* Geometric mean; ** Range

RESULTS AND DISCUSSION

Average recoveries of 81 and 91% were obtained for Pb and Cd respectively. These low recoveries may be attributed to the high carbon content of the samples and its high adsorption power. Retention losses are also possible as silica crucibles have been shown to retain an average of 16% Pb (Ajayi et al 2001; Gorsuch, 1959). The mean (± SD) Pb and Cd content of the dry cells studied is 1077.9±751.7mg/kg (Range 42 – 3170mg/kg) and 108.29±81.41mg/kg (Range 4.6 – 410mg/kg) respectively. Because of the skewed nature of the results obtained, the data was normalized by logarithmic transformation by calculating the geometric mean. A summary of the result obtained according to the sizes of the dry cells is shown in Table 2. The dry cells are grouped according to the type of the outer cover and into 'Cd-free cells' and 'normal cells' following indications on their labels (Table 3) The mean Pb content of dry cells with non-metal cover (1325.0±857.3mg/kg) is significantly higher ($p<0.005$)than the corresponding value for the dry cells with metal cover (682.5 ±307.2mg/kg).Similarly, the mean Cd content of the dry cells with non-metal cover (141.9± 82.3mg/kg) is significantly higher ($p<0.005$) than those of the dry cells with metal cover (54.5±47.9mg/kg),Table 3. This may indicate that dry cells with improved packaging are more environment friendly. In Nigeria dry cells with metal cover are on the average 25% costlier. This improved metal outer packaging reduces leakages even on abusive use of the dry cells.

Table 3. Comparison of the different groups of dry cell batteries (mg/kg)

Group	Pb	Cd	N
Batteries with metal cover	682.47 ± 307.22 (591.37)* 100 - 1126**	54.49 ± 47.87 (33.22) 4.6 - 174.9	15
Batteries with non-metal cover	1325.04 ± 867.31 (910.27) 42. - 3170	141.91±82.32 (120.27) 23 - 410	24
Cd-free batteries	919.38 ± 660.72 (644.69) 100 - 2135	89.60 ± 60.54 (53.06) 4.6 - 174.9	13
Batteries not indicated as Cd-free	1157.15 ± 807.68 (843.4) 42. - 3170	117.63 ± 90.50 (86.21) 8.1 - 410	26

* Geometric mean; **Range

About a third of the dry cells studied (36%) were imported from China Mainland. The higher mean Pb and Cd contents of these Chinese dry cells compared to cells from other countries (Tables 4) may be explained by the observation that more than 90% of these cells have non-metal outer cover. The mean Pb and Cd content of the dry cells labeled 'Cd-Free' (919.4±660.7mg/kg and 89.6±60.5mg/kg respectively) are lower than the corresponding values for the 'normal cells'. This is however not statistically significant. The mean Pb and Cd values of the 'Cd-Free' cells with metal cover (724.0±389.9mg/kg and 52.4±63.2mg/kg respectively) are also lower than the values for the 'Cd –free' cells without metal cover (980.7±813.8mg/kg and 133.0±20.0mg/kg respectively). It was observed that three (3) 'Cd-free' cells of the same brand (different sizes) have mean Pb and Cd values of 743.7mg/kg and 33.7mg/kg respectively. This low mean Cd value appears to indicate a true reduction in the Cd content of this brand. This may indicate the industrial application of the extensive research at reducing/eliminating and finding alternatives to the use of Hg and Cd in dry cells manufacture. The country of origin of this brand of dry cells in however not indicated on the label. A weak, albeit significant, positive correlation was found between the Pb and Cd contents of the dry cells ($r = 0.398$, $p<0.02$). This corroborates the result of a study in the vicinity of an automotive battery manufacturing company in Nigeria (Onianwa & Fakayode, 2000). This positive correlation indicates that the estimated regression model of the data obtained, Cd = 61.67 + 0.043 (Pb) can explain only about 16% of the variation in the data obtained ($R^2 = 0.16$). This model therefore is insufficient to give accurate predictions. The highest Pb and Cd values (3170mg/kg and 410mg/kg respectively) were obtained in dry cells imported from China (Table 4) The Pb and Cd contents of the only surviving local Nigerian brand are 408mg/kg and 34.5mg/kg. The dry cell from the United States contains 303mgPb/kg and 11.1mgCd/kg which are lower than the corresponding values for dry cells from Nigeria, and elsewhere. The Pb and Cd content of the Nigerian brand are also lower than the mean Pb and Cd values for dry cells from China, Indonesia, Japan, Korea and Spain (Table 4). About 15 billion batteries are produced in China yearly with about 10 batteries per person per year in China. At present more than 60% of the Nigerian primary battery trade is controlled by China.

In the US, about 2.5 billion household batteries are purchased each year. More than 90% of this is single use batteries that find their way into landfills and incinerators. The US-EPA estimated that in 1989, 88% of the 1.4 million pounds (635 metric tonnes) of Hg in urban trash in the US came from single-use batteries (Schwartz et al., 1994).One major concern is that the heavy metals contained by dry cells could leach from landfills into ground water, or shift to fly ash at open waste minimization/burning sites or at waste-to-energy plants (Nakamura, 1996; Malloy, 1994). The management of Ni-Cd rechargeable batteries is a problem that has assumed a global dimension (Rydh and Karlstrom, 2002). In Nigeria, Ni-Cd batteries, auto-rechargeable batteries and primary battery wastes are disposed with municipal waste. Nigeria does not have any integrated framework regarding the monitoring and management of toxic and hazardous materials and wastes. Limited funding has also caused significant impediments to the effective management of toxic and hazardous wastes. Apart from scarcity of financial resources, there has not been any development of appropriate technology following the principles of waste minimization and sustainable development. Any interim effort to halt this form of metal pollution in Nigeria must include the proper financing and management of waste, and the provision of basic infrastructure to halt the open burning of waste in inhabited area. Long term control measures will include legislating and enforcing the removal of dry cells and similar toxic products from wastes to be incinerated and the setting-up of national standards for the levels of heavy metals in dry cells.

Table 4. Summary of lead and cadmium contents of dry cell batteries from various countries (mg/kg dry weight)

Country	N	Lead		Cadmium	
		Mean	Range	Mean	Range
China	14	1368.36±1005.35 (846.78) *	42-3170	151.47±102.44 (127.51) *	30 - 410
Indonesia	2	1032±39.61 (1006.95)	806-1258	84.4±18.67 (83.36)	71.2-97.6
Japan	5	715.2±479.97 (548.65)	168-1295	131.48±24.51 (129.62)	104.9-160
Korea	2	1137.5±911.46 (937.3)	493-1782	81.45±101.75 (38.17)	9.5-153.4
Malaysia	1	709	-	12.5	-
Spain	1	702	-	65.8	-
USA		303	-	11.1	-
Nigeria		408	-	34.5	-
Source not Indicated	12	1070.33±592.82 (853.4)	100-2135	82.47±63.04 (50.14)	4.6-182.5
Entire Study	39	1077.9±751.7 (771.13)	42-3170	108.29±81.41 (73.33)	46-410

* Geometric mean

REFERENCES

Ajayi, S O; Osibanjo, O (1981). Pollution studies on Nigeria rivers II. Water quality of some Nigerian rivers. Environ Pollut (Series B) 2: 87-95.

Ayres, R U; Ayres, L W (1994). Consumptive uses and losses of toxic heavy metals in the United Sates, 1880-1980. In: Industrial metabolism: restructuring for sustainable development (Ayres R.U and Simonis U.E Eds.) United Nations University Press, New York, p 259-295.

Bader, M; Dietz, M C; Ihrig, A; Triebig, G (1999). Biomonitoring of manganese in blood, urine and axillary hair following low-dose exposure during the manufacture of dry cell batteries. Int Archives of Occup and Environ Health. 72 (8): 521-527.

Fergusson, J E; Hibbard, K A; Ting, R L H (1981). Lead in human hair: General survey-battery factory employees and their families. Environ Pollut 2: 235-248.

Gorsuch, T T (1959). Radiometric investigation and recovery for analysis of trace elements in organic and biological materials. Analyst 84:135-172.

Lai, J S; Wu, T N; Liou, S H; Shen, C Y; Guu, C F;Ko, K N;Yun, C H;Chang, P; Guu, C F; Ko, K

N;Yun, C H;Chang, P Y (1997). A study of the relationship between ambient lead and blood among lead battery workers. Int Arch Occup Environ Health 69 (4): 295-300.

Malloy, M (1994). Handling difficult materials: batteries. Waste Age 25 (9):117-120.

Nakamura, K; Kinoshita, S; Takatsuki, H. (1996). The origin and behavior of lead, cadmium and antimony in MSW incinerator. Waste Mgt. 16 (5-6):509-517.

Nwankwoala, A U; Osibanjo, O (1992). Baseline levels of selected organochlorine pesticide residues in surface waters in lbadan (Nigeria) by electron capture gas chromatography. Sci Total Environ 119:179-190.

Oleru, U G; Elegbeleye, O O; Enu, C C; Olumide, Y M (1983). Pulmonary function and symptoms of Nigerian workers exposed to carbon black in dry cell battery and tire factories. Environ Res 30: 161-168.

Onianwa, P C; Fakayode, S O (200). Lead accumulation of topsoil and vegetation in the vicinity of a battery factory in Nigeria. Environ Geochem Health 22: 211-218.

Ozaki, H; Sharma, K; Phanuwan, C; Fukussi, K; Polprasert, C (2003). Management of hazardous waste in Thailand: Present situation and future prospects. J Material Cycles Waste Mgt. 5 (1): 31-38.

Ritcher, E D; Yaffe. Y; Gruener. N (1979). Air and blood lead levels in a battery factory. Environ Res 20:87-98.

Rydh, C J; Karlstrom, M (2002). Life cycle inventory of recycling portable nickel-cadmium batteries. Resources, Conservation and Recycling 34:289-309.

Schwartz, A T; Bunce, D M; Sillerman, R G; Stanitski, C L; Stratton, W J;Zipp, A P (1994). Chemistry in context: Applying chemistry to society (American Chemical Society project) Wm. C Brown Pub. p 251-252.

Semu, E; Singh, B R; Selma-Olsen, A R (1996). Mercury pollution of effluent, air and soil near a battery factory in Tanzania. Water, Air Soil Pollut 27:141-146.

Shapek, R A (1996). Dry cells battery, health and environmental hazards and disposal options. J Solid Waste Technol. Mgt 23 (1): 53-64.

Smith, D R; Flegal, A R (1995). Lead in the biosphere; recent trends. Ambio, 24(1): 21-23.

Sridhar, M K C; Bammeke, A O (1986). Heavy metal contents of some solid wastes in Ibadan, Nigeria. Water, Air Soil Pollut 29:51-56.

Ward, N I; Roberts, E; Brooks, R R (1977). Lead pollution from a New Zealand battery factory and smelter compared with that from motor-vehicle exhaust emissions. New Zealand J of Sci 20:407-412

Wohl, A R; Dominguez, A; Flessel, P (1996). Evaluation of lead levels in children living near a Los Angeles country battery recycling facility. Environ Health Perspect 4 (3):314-317.