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Determination of Co, Li, Mn and Ni Levels of Waste Rechargeable Batteries Collected from Aba, Nigeria

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Abstract

The consumption of portable rechargeable batteries has increased since the introduction of mobile telecommunication and other portable electronics. This study assessed the levels of Co, Li, Mn and Ni in rechargeable batteries, and estimated recoverable metals from battery importation in Nigeria and the financial benefits of locally recycling them. Metal levels in the electrode materials of spent batteries were determined using AAS after digestion using acid mixture (2:1 HCl and HNO_3). For Li-ion batteries, the results of Co, Li, Mn and Ni in the battery electrodes (mean ± standard deviation) are 28899±5277 mg/kg (range 33397-14706 mg/kg), 65961±8490 mg/kg (81159-47132 mg/kg), 18310±4961 mg/kg (32549-8821 mg/kg) and 24329±12271 mg/kg (35857-3808 mg/kg) respectively. Results for Li-polymer batteries are 29753±4649 mg/kg (range 33555-17743 mg/kg) for Co, 65477±5293 mg/kg (73284-55494 mg/kg) for Li, 21287±6628 mg/kg (30260-8461 mg/kg) for Mn and 20159±10120 mg/kg (32706-2766 mg/kg) for Ni. Corresponding values for NiMH are 66287±7487 mg/kg (71581-60993 mg/kg) for Co, 13851±2455 mg/kg (15587-12115 mg/kg) for Li, 32899±30689 mg/kg (54605-11192 mg/kg) for Mn and 82735±2610 mg/kg (84580-80889 mg/kg) for Ni. All Co, Mn and Ni exceeded the toxicity threshold limit concentration values (Co: 8000 mg/kg and Ni; 2000 mg/kg) indicating that these batteries should be treated as hazardous wastes. Import data from UN Comtrade showed that 2.6 million tonnes of lithium-ion and 4351 tonnes of mobile phone batteries were imported into Nigeria between 1999 and 2022. If the waste batteries are collected and recycled, the recoverable metals are worth US$6 Million and US$9914 respectively.

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This shows that much forex can be obtained from waste batteries if collected, recycled and sold in the mineral market. If disposed with municipal waste, they will contaminate the environment; endangering the lives of plants, animals and humans.

Keywords: Heavy metals; lithium; batteries; Nigeria; recycling.

1. Introduction

In an era dominated by portable electronics, the proliferation of rechargeable batteries has led to a surge in electronic waste (e-waste) due to their limited lifespan and improper disposal practices [1, 2]. Electronic waste, commonly referred to as e-waste, is used to describe discarded electronic devices that have reached the end of their useful life. They include a wide range of items such as computers, laptops, smartphones, tablets, digital cameras and other electronic appliances. They are mostly generated when older electronic devices become outdated and are replaced by newer, more advanced models. Some electronic devices have relatively short lifecycle due to rapid technological advancements or built – in- obsolescence, some may become non – functional due to technical issues, damages, or wear and tears. Also, upgrade of these electronic devices may necessitate a change and disposal of older ones. E-waste poses environmental and health risks if not managed properly [3]. While rechargeable batteries are designed to be reusable through multiple charging cycles, they eventually reach a point where their capacity diminishes and they need to be replaced. Waste rechargeable batteries become a part of e-waste at their end-of-life; when they are thrown into the regular trash, they may end up in landfills, where they can pose environmental risks. Also, these rechargeable batteries contain toxic substances that can leach into soil and water, leading to environmental contamination. E-waste not only poses environmental and health risks but also represents a potential loss of valuable resources contained within these discarded batteries [4, 5]. Among the key components of lithium-ion, lithium-polymer and nickel-metal hydride rechargeable batteries are valuable metals such as lithium, cobalt, nickel, and rare earth elements [6]. These metals play a pivotal role in the functionality and performance of batteries, making them indispensable for various applications [3]. However, the conventional disposal methods of e-waste, often characterized by incineration and landfilling, not only squander these precious resources but also contribute to environmental pollution and resource scarcity [4, 7]. As society moves towards more sustainable practices, there is a pressing need to develop efficient and environmentally sound methods for the recovery of valuable metals from waste rechargeable batteries [6]. The field of battery recycling and metal recovery has gained momentum in recent years, driven by concerns over resource depletion, environmental impact, and the economic potential of recycling these materials [8, 9]. Waste rechargeable batteries from portable electronics, such as smartphones, tablets, laptops, and cameras, are a complex composition of materials designed to store and discharge electrical energy efficiently. The lithium-ion batteries consist of several key components, each serving a specific function and requiring careful management during recycling or disposal to minimize environmental impact [10]. The cathode is typically composed of lithium cobalt oxide ($LiCoO_2$) in lithium-ion batteries, and various other materials like lithium iron phosphate ($LiFePO_4$) or nickel-cobalt-manganese (NCM) compounds in newer-generation batteries. These materials are responsible for storing positively charged lithium ions during charging and releasing them during discharge [11]. In Ni-MH batteries, the cathode materials are nickel - hydrogen alloys of rare earth metals such as neodymium (Ne), lanthanum (La), praseodymium (Pr) and cerium (Ce) [12]. The anode of lithium-ion batteries is commonly made of graphite, which allows for the intercalation of lithium ions during charging. In some cases, silicon-based anodes may be used for their higher capacity but require more careful handling while NiMH batteries have nickel oxides and hydroxides as anode. Lithium-ion batteries contain a liquid or solid electrolyte, facilitating the movement of lithium ions between the anode and cathode during charging and discharging. Liquid electrolytes typically consist of lithium salts dissolved in a solvent, while solid-state electrolytes are becoming more prevalent due to their safety advantages. A separator made of a porous material, often polyethylene or polypropylene, physically separates the cathode and the anode to prevent short circuits while allowing the passage of ions [13]. Thin foils made of aluminum and copper serve as current collectors on the cathode and anode sides, respectively, helping to conduct electricity in and out of the battery. The battery is enclosed in a metal or plastic casing to protect it from physical damage and environmental exposure. In portable electronics, batteries usually include protection circuitry to control voltage and current, preventing overcharging, over-discharging, and overheating, which could lead to safety hazards. Various adhesives, insulators, and separators are used to hold the components together, maintain insulation, and ensure structural integrity. Lithium-ion (Li-ion), nickel-metal hydride (Ni-MH), and lithium-polymer (Li-poly) batteries all contain valuable metals and materials that can be recovered through recycling processes. Spent LIBs contain valuable metals like cobalt (5-20 %), nickel (5-10 %) and lithium (5-8 %) and the Ni-MHs are rich in nickel (36-42 %), cobalt (3-5 %), and REEs (5-25 %) [14].

2. Materials and Methods

2.1. Sample Collection

Spent rechargeable batteries were collected from mobile phone and laptop repairers and users from a major repair hub located at Hospital Road and St Michaels Road by Asa Road, both in Aba and some from phone users, photographers, microphone users and repairers also within Aba. The batteries that were collected were lithium – ion, lithium-polymer and nickel - metal hydride batteries and were of different brands. A representative sample of 53 Li-ion, 30 Li-polymer and 8 Ni-MH batteries were selected. They were produced between 2013 and 2023 and used laptops, MP3, microphones and mobile phones.

2.2. Sample Preparation

The individual weights of the batteries were taken. Other data that were collected on the individual batteries were their types, years of production, countries of production, disposability, recyclability etc. They were finally grouped into 34 samples of which 22 were Li-ion, 10 were Li-polymer and 2 were NiMH (all comprising of 22 single and 12 pooled samples). The batteries were soaked in salt solution (NaCl solution) for 24 hours to ensure a complete discharge 11]. Then they were washed thoroughly with clean distilled water and heated at 60 ^oC in a hot air oven (Yamato Scientific DGS400 Oven) for 2 hours to dry [15, 16]. Using a pair of scissors and pliers, the batteries were disassembled. Plastic and metal casings were removed to separate the electrode materials (cathode and anode materials) and the separators [16, 4].

2.3. Sample Digestion

The digestion flasks were each soaked with 10 % HNO_3 solution. Then they were rinsed with deionized water and dried in hot air oven at 60 ^{0}C for 90 mins. Other glass wares were washed thoroughly with soap and tap water and left to dry.A known weight (2.0 g) of the cut electrode materials was weighed into the digestion flask. Also, 5 ml of 65 % nitric acid and 10 ml of 70 % hydrochloric acid was added into the digestion flask and placed on the heating mantle/digester in a fume hood at 120 ^{0}C. On addition of acid, some of the samples changed color to greenish blue and then to maroon red when distilled water was added and allowed to boil. Brown fumes started to appear and escaped through the mouth of the digestion flask as heating began which completely disappeared after about an hour. Thereafter, 20ml of distilled water was added and allowed to boil for 10 minutes. It was brought down and allowed to cool. It was then filtered into a 50 ml flask using a Whatmann filter paper (the filtrate was about 25 ml). The filtrate was then marked up to 50 ml with distilled water and subjected to an Atomic Absorption Spectroscopy.

2.4 Measurement of Metals in the Digests

Valuable metals namely; Co, Li, Mn and Ni were detected and their concentrations determined by atomic absorption spectroscopy. Standard solutions with known concentrations of the studied metals were prepared. The AAS was turned on to warm up for a few minutes. The acetylene gas and the compressor were turned on. After venting the air, then the flow valve was turned on. The computer was turned on and the software launched and allowed to warm up for 30 minutes to stabilize the light source for optimal performance. The instrument status was checked to know if the lamp was properly positioned and if the current was good for use. Distilled water was first aspirated for 5 minutes to allow the system to warm up. The metal of interest was selected, the flame was turned on and the calibration blank was aspirated. The prepared standards were aspirated and the absorbance of each standard solution was measured. A calibration curve was plotted by plotting Absorbance value against the known Concentrations of the standards. Sample blank was aspirated after the calibration. The sample digests were aspirated using a nebulizer and the absorbance was measured at the absorption wavelengths of the metals.

2.5. Quality Control and Data Analysis

Adequate quality control measures were included in the study. Instruments were calibrated using standards while all glass and plastic-wares were cleaned properly and soaked in 10% HNO_3 overnight, then rinsed with distilled water before use. ANALAR grade reagents and deionized water were used. SPSS 10 was used for data analysis. Blanks were also employed.

3. Results and Discussion

3.1 Variation in Metal Contents of the Battery Types Studied

The Figure 1 is a distribution of the concentration of valuable metals (cobalt, lithium, manganese and nickel) in the battery samples analyzed. The raw data was derived from [17]. The concentration of Li was significantly high in most samples except samples 31 and 32 where it dropped before rising again. This shows that most of the batteries were lithium-ion and lithium-polymer batteries. At the same point where lithium level was low, nickel rose significantly. Co and Mn had same range of concentration while nickel sharply shot up and came down intermittently hitting zero concentration at some points. It also shows a high concentration of cobalt in samples 31 and 32 which are NiMH batteries. The fluctuations in the concentrations may have been informed by the battery sizes. This implies that the recycling of lithium batteries can produce a large quantity of lithium while cobalt and nickel can be gotten from NiMH batteries in large quantities.

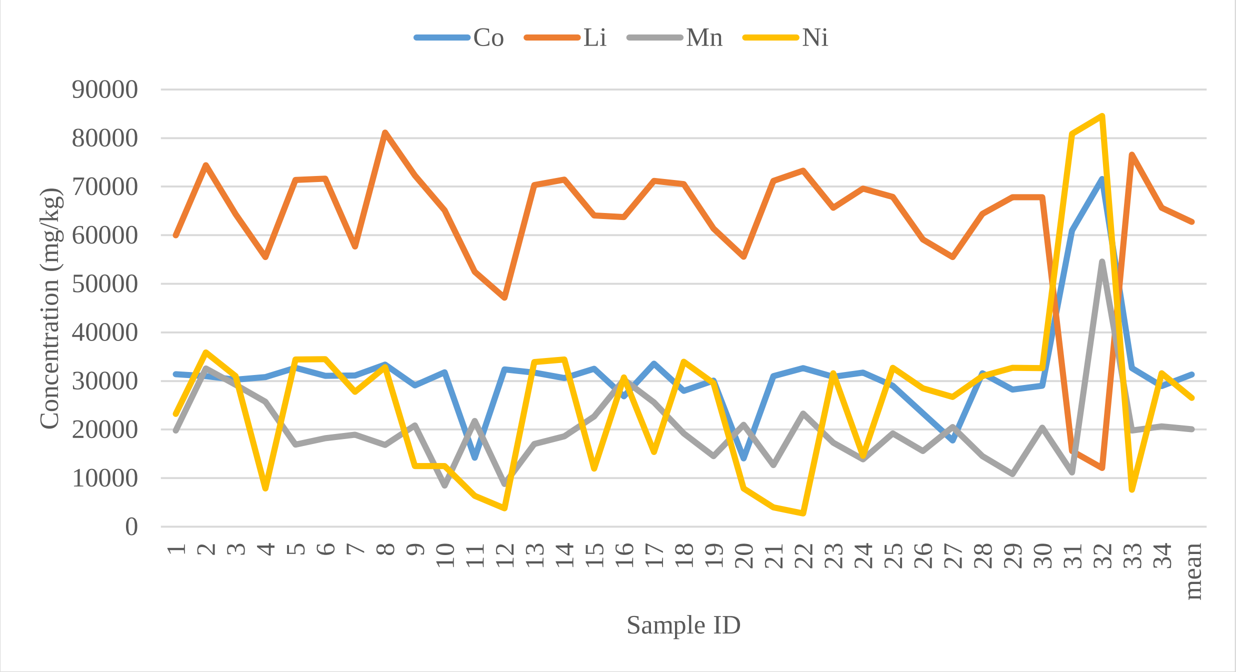

Figure 1: Variation in metal contents of the batteries irrespective of the battery chemistry

3.2 Metal Contents According to Battery Type

The summaries of the metal contents of Li-ion batteries, Li-polymer batteries and NiMH batteries are presented in Tables 1, 2 and 3 respectively. A comparison of the average metal contents of the three battery types is presented in Figure 2.

The metal concentrations ±standard deviation (range) of the sample lithium-ion batteries are 28899±5227 mg/kg (33397-14076 mg/kg) for Co, 65961±8490 mg/kg (81159-47132 mg/kg) for Li, 18310±4961 mg/kg (32549-8821 mg/kg) for Mn and 24329±12271 mg/kg (35857-3808 mg/kg) for Ni. Li has the highest concentration while Mn has the least. The high standard deviation and range values are likely informed by the differences in factory specifications, sizes and battery applications.

The metal concentrations ±standard deviation (range) of the sample lithium-polymer batteries are 29753±4649 mg/kg (33555-177436 mg/kg) for Co, 65477±5293 mg/kg (73284-55494 mg/kg) for Li, 21287±6628 mg/kg (30260-8461 mg/kg) for Mn and 20159±10120 mg/kg (32706-2766 mg/kg) for Ni. Li has the highest concentration while Mn has the least. The high standard deviation and range values such as in li-ion are likely informed by the differences in factory specifications, sizes and battery applications.

The distribution of metal concentrations ±standard deviation (range) of the sample nickel metal hydride batteries are 66287±7487 mg/kg (71581-60993 mg/kg) for Co, 13851 ±2455 mg/kg (15587-12115 mg/kg) for Li, 32899±30698 mg/kg (54605-11192 mg/kg) for Mn and 82735±2610 mg/kg (84580-80889 mg/kg) for Ni. Ni has the highest concentration while Li has the least. The standard deviation of manganese is very high indicating a likely human or measurement error. Range values are wide and possibly informed by factory production specifications.

Table 1: Summary of metal levels of lithium-ion sample batteries

Parameter	Co	Li	Mn	Ni
Mean	28899	65961	18310	24329
Standard deviation	5227	8490	4961	12271
Maximum	33397	81159	32549	35857
Minimum	14076	47132	8821	3808
Geometric mean	28264	65409	17671	19513

Table 2: Summary of metal levels of lithium- polymer sample batteries

Parameter	Co	Li	Mn	Ni
Mean	29753	65477	21287	20159
SD	4649	5293	6628	10120
Maximum	33555	73284	30260	32706
Minimum	17743	55494	8461	2766
Geometric mean	29337	65280	20129	16803

Table 3: Summary of metal levels of NiMH sample batteries

Parameter	Co	Li	Mn	Ni
Mean	66287	13851	32899	82735
Standard deviation	7487	2455	30698	2610
Maximum	71581	15587	54605	84580
Minimum	60993	12115	11192	80889
Geometric mean	66075	13742	24721	82714

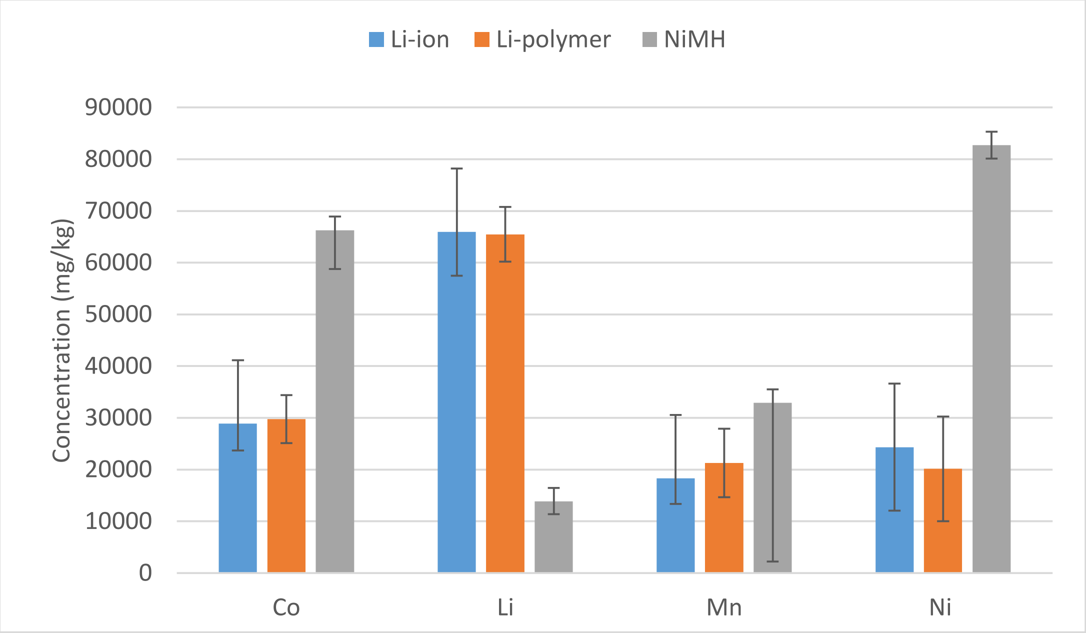

Figure 2: Comparison of the average metal contents of the three battery type
(Note: Error bars are standard deviation)

Higher Li was observed in Li-ion and Li-polymer batteries. In fact, the Li content of Li-ion and Li-polymer batteries were approximately five (5) times that of the NiMH batteries. The Co contents of the NiMH batteries were about twice that of the Li-ion and Li-polymer batteries. Also, the Ni contents of the NiMH batteries were about three times that of the Li-ion batteries and four times that of the Li-polymer batteries. The Mn concentrations did not vary much even though more Mn were observed in the NiMH batteries

3.3 Metal Contents According to Country of Manufacture

Most of the batteries studied were manufactured in China while a few were manufactured in Hong Kong and Japan. Presented in Table 4 is a summary of the metal concentrations in batteries manufactured in China. The distribution of metal concentrations ±standard deviation (range) of the sample batteries manufactured in China are 31880±10195 mg/kg (71581-14076 mg/kg) for Co, 62870 ±14726 mg/kg (81159-12115 mg/kg) for Li, 19811±8621 mg/kg (54605-8461 mg/kg) for Mn and 29125±17767 mg/kg (84580-2766 mg/kg) for Ni.

Presented in Table 5 is a summary of metal concentrations (mg/kg) for valuable metals in sample batteries manufactured in other countries. The distribution of metal concentrations ±standard deviation (range) of the sample batteries manufactured in other countries are 25867±10140 mg/kg (32616-14207 mg/kg) for Co, 61542 ±13135 mg/kg (76608-52497 mg/kg) for Li, 22448±3017 mg/kg (25739-19813 mg/kg) for Mn and 7270±776 mg/kg (7844-6388 mg/kg) for Ni. A comparison of the metal contents of batteries manufactured in China and those manufactured in other countries is presented in Figure 3.

Table 4: Summary of valuable metal levels of batteries manufactured in China (mg/kg)

Parameter	Co	Li	Mn	Ni
Mean	31880	62870	19811	29125
Standard deviation	10195	14726	8621	17767
Geometric mean	30667	59540	18412	23222
Maximum	71581	81159	54605	84580
Minimum	14076	12115	8461	2766

Table 5: Summary of valuable metal levels of batteries manufactured in other countries (mg/kg)

Parameter	Co	Li	Mn	Ni
Mean	25867	61542	22448	7270
Standard deviation	10140	13135	3017	776
Geometric mean	24251	60668	22316	7242
Maximum	32616	76608	25739	7844
Minimum	14207	52497	19813	6388

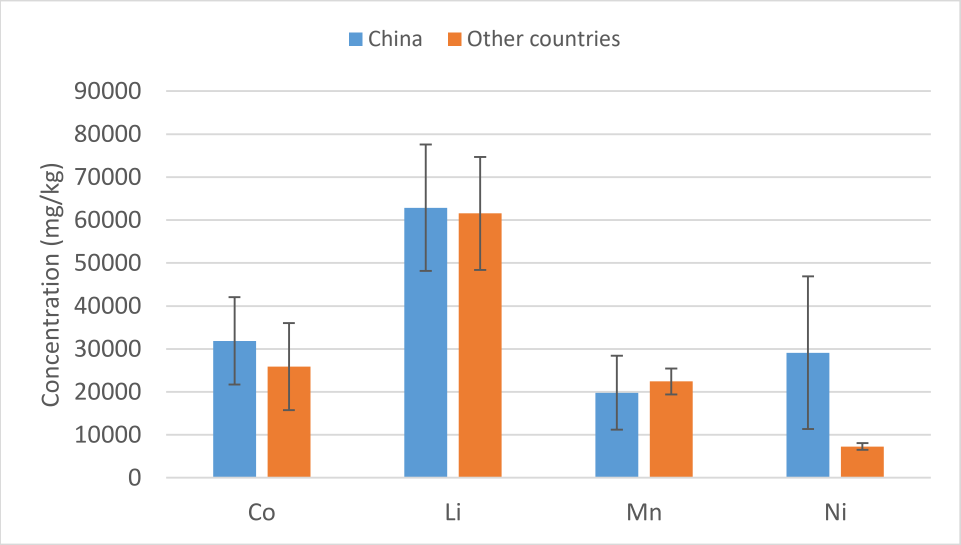

Figure 3: Comparison of metal contents of batteries manufactured in China and other countries

(Note: Error bars are standard deviation)

From Figure 3, sample batteries made in China had higher mean concentrations of cobalt, lithium and nickel but a slightly lower mean concentration of manganese than those manufactured in other countries. This shows that most of the batteries manufactured in China were lithium-ion and lithium-polymer batteries. Also, their high concentration of nickel shows that the nickel metal hydride sample batteries were also manufactured in China.

3.4 Metal Contents According to Battery Application

Presented in Table 6, Table 7 and Table 8 are a summary of the metal levels of batteries according to their various applications for mobile phone batteries, microphone batteries and laptop batteries respectively. The distribution of metal concentrations ±standard deviation (range) of the sample mobile phone batteries shown in Table 6 are 29086±5211 mg/kg (33555-14076 mg/kg) for Co, 65373±7656 mg/kg (81159-47132 mg/kg) for Li, 19462±5667 mg/kg (32549 -8461 mg/kg) for Mn and 22929±11646 mg/kg (35857-2766 mg/kg) for Ni. This shows a high concentration in lithium and cobalt implying that the recycling of mobile phone batteries can yield large quantities of lithium and cobalt which has a high economic value.

Also, the distribution of metal concentrations ±standard deviation (range) of the sample microphone batteries shown in Table 7 are 66287±7487 mg/kg (71581-60993 mg/kg) for Co, 13851 ±245 5 mg/kg (15587-12115 mg/kg) for Li, 32899±30698 mg/kg (54605-11192 mg/kg) for Mn and 82735±2610 mg/kg (84580-80889 mg/kg) for Ni. This shows very high concentrations in nickel and cobalt implying that the recycling of mobile phone batteries can yield large quantities of nickel and cobalt which has a high economic value. Also, proper handling of these waste batteries is required because they are highly toxic.

In addition, the distribution of metal concentrations ±standard deviation (range) of the sample laptop batteries shown in Table 8 are 30786±2589 mg/kg (32616-28955 mg/kg) for Co, 71119±7763 mg/kg (76608-65630 mg/kg) for Li, 20220±576 mg/kg (20627-19813 mg/kg) for Mn and 1960±17000 mg/kg (31620-7579 mg/kg) for Ni. The laptop batteries have the highest mean concentration of valuable metals possibly because they power a heavy portable electronic equipment. This promises a high metal and economic yield.

Only a single sample battery used in MP3 was studied and it contained 28237 mg/kg of Co, 67844 mg/kg of Li, 10851 mg/kg of Mn and 32683 mg/kg of Ni. Figure 4 represents the summary of metals in batteries according to their applications.

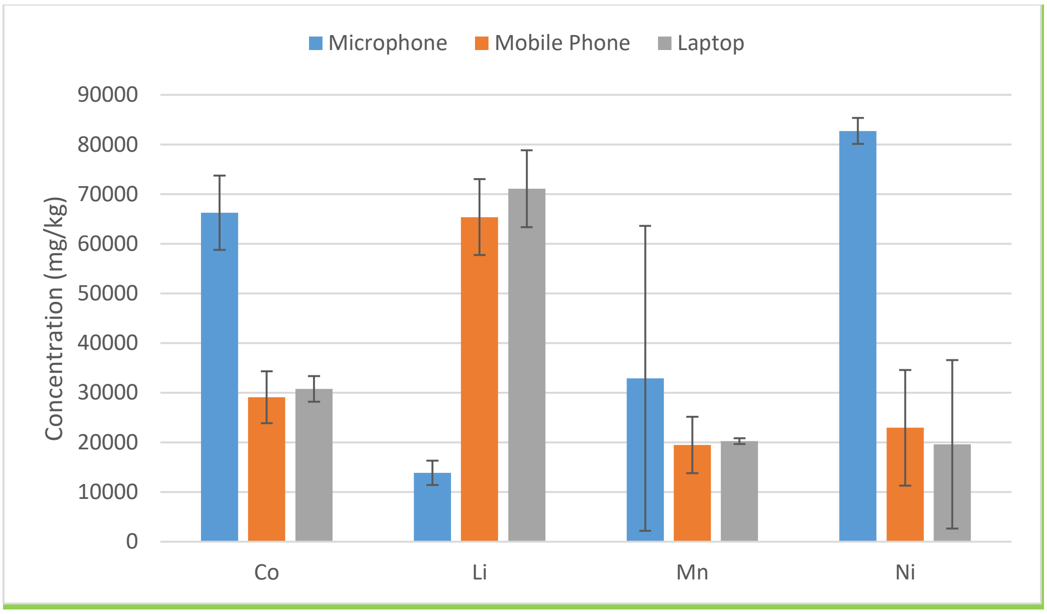

Figure 4: Summary of metals in batteries according to their applications

(Note: Error bars are standard deviation)

Table 6: Summary of metal levels of mobile phone batteries

Parameter	Co	Li	Mn	Ni
Mean	29086	65373	19462	22929
Standard deviation	5211	7656	5667	11646
Geometric mean	28466	64920	18623	18499
Maximum	33555	81159	32549	35857
Minimum	14076	47132	8461	2766

Table 7: Summary of metal levels of microphone batteries

Parameter	Co	Li	Mn	Ni
Mean	66287	13851	32899	82735
Standard deviation	7487	2455	30698	2610
Geometric mean	66075	13742	24721	82714
Maximum	71581	15587	54605	84580
Minimum	60993	12115	11192	80889

Table 8: Summary of metal levels of Laptop batteries

Parameter	Co	Li	Mn	Ni
Mean	30786	71119	20220	19600
Standard deviation	2589	7763	576	17000
Geometric mean	30731	70907	20216	15481
Maximum	32616	76608	20627	31620
Minimum	28955	65630	19813	7579

3.5 Metal Contents According to Year of Battery Manufacture

The sample batteries used for this study were manufactured within a space of ten (10) years between 2013 and 2023. Presented in Table 9 is a summary of the metal concentrations in the sample batteries manufactured from 2013-2017 (Table 9); 2018-2023 (Table 10).

The distribution of metal concentrations ±standard deviation (range) of the sample batteries manufactured from 2013-2017shown in Table 4.12 are 26871±5855 mg/kg (32616-17743 mg/kg) for Co, 64255±7855 mg/kg (76608-55494 mg/kg) for Li, 18765±1418 mg/kg (20506-16921 mg/kg) for Mn and 18874±9473 mg/kg (30056-7579 mg/kg) for Ni. This shows a high concentration in lithium and cobalt implying that they were mostly lithium-ion and lithium-polymer batteries. The propensity for a high recovery of lithium and cobalt is evident from recycling. Nickel and manganese can also be recovered in smaller quantities thereby contributing to economic recovery.

The distribution of metal concentrations ±standard deviation (range) of the sample batteries manufactured between 2018-2023 shown in Table 4.13 are 33762±8652 mg/kg (48927-27408 mg/kg) for Co, 58977±18117 mg/kg (69527-26733 mg/kg) for Li, 20718±6184 mg/kg (29197-14501 mg/kg) for Mn and 35229±12907 mg/kg (57286-23171 mg/kg) for Ni. The mean concentrations of the recoverable metals are not so high because this group is a mixture of the three battery chemistries. However, these metals can still be recovered in moderate quantities

Table 9: Summary of metal contents (mg/kg) of batteries manufactured between 2013-2017

Parameter	Co	Li	Mn	Ni
Mean	26871	64255	18765	18874
Standard deviation	5855	7855	1418	9473
Geometric mean	26295	63885	18722	16770
Maximum	32616	76608	20506	30056
Minimum	17743	55494	16921	7579

Table 10: Summary of the metal content (mg/kg) of batteries manufactured between 2018-2023

Parameter	Co	Li	Mn	Ni
Mean	33762	58977	20718	35229
Standard deviation	8652	18117	6184	12907
Geometric mean	33012	55761	20002	33635
Maximum	48927	69527	29197	57286
Minimum	27408	26733	14501	23171

3.6 Comparison with Regulatory Limits of Metals in Plastic

The results of this study were compared with limits used to classify waste materials as toxic such as the TTLC (Toxicity Threshold Limit Concentration), USEPA (United States Environmental Protection Agency) and EU (European Union) Allowable Limits. Presented in Table 11 are the mean values of metals alongside TTLC, EPA and EU allowable limits

The results of this study were compared with TTLC, EPA and EU regulatory thresholds for Co, Li, Mn and Ni. The deduction was that cobalt concentration of Li-ion and Li-polymer batteries is about 3 and half times its toxicity threshold (8000 mg/kg) and NiMH contains about 8 and half times. Also, comparing with USEPA allowable limits for cobalt (250 mg/kg), Li-ion, Li-polymer and NiMH electrode materials contain about 116,119 and 265 times in concentration respectively. Furthermore, Li-ion, Li-polymer and NiMH batteries contain about 24, 28 and 44 times respectively, the allowable limits of USEPA, while for EU, the concentrations are about 240, 280 and 440 times respectively of the allowable limits. For nickel, Li-ion, Li-polymer and NiMH batteries contain 12, 10 and 41 times the TTLC threshold respectively; 43, 36 and 148 times the USEPA allowable limits respectively and 324, 269 and 1103 times the EU allowable limits. Lithium is not regarded as a hazardous substance at the level in which it is found in the soil, hence, no stated allowable limits. The results above indicate that rechargeable batteries contain hazardous substances and can pose a great risk to lives (plants, animals and humans) and the environment if not properly handled.

Table 11: Comparison of mean values of metals with TTLC, EPA and EU allowable limits

Battery Chemistry	Co content (mg/kg)	Ni content (mg/kg)	Li content (mg/kg)	Mn content (mg/kg)
Li-ion	28899	24329	65961	18310
Li-polymer	29753	20159	65477	21287
NiMH	66287	82735	13851	32899
TTLC	8000	2000	-	-
EPA	250	560	-	750
EU	-	75	-	75

3.7 Comparison of Results with Literature

Presented in Table 12 are the results from some previous researches done on the determination of the concentrations of valuable metals from lithium batteries and nickel metal hydride rechargeable batteries as well as the results of this research.

The results of the study show some closeness with recent researches. For NiMH, the Ni content is highest as expected with the value of 82735 mg/kg which is close to 75272 mg/kg as determined by [18]. Co concentration derived as 66287 mg/kg is equally high as obtained by Liu *and his colleagues*, 2019 (55900 mg/kg), same applies to Mn (32899 mg/kg) , which is similar to 30200 mg/kg obtained by Liu and his colleagues, 2019. For li-ion and li-polymer batteries which fall into the category of lithium batteries (LIBs), Li has the highest concentration (65961 and 65477 mg/kg). This has close values with results from Zhou *and his colleagues*; 2021 (50000-70000 mg/kg) , 51600 mg/kg from [6] and 70400 mg/kg from [20]. Also, results of Mn concentration (18310 and 21287 mg/kg) are closely related to the findings of [14] (18700 mg/kg) as well as Ni concentration (24329 and 20159 mg/kg) which [14] also determined as 29900 mg/kg. However, there is considerable reduction in the use of Co in the manufacture of electrode materials of PEDs as significantly reflected in the research results. In previous researches, Co concentration in LIBs ranged from 50000-311800 mg/kg but this research result shows (28899 and 29753 mg/kg). This could be as a result of technological innovations towards the reduction in the cobalt content or complete withdrawal of cobalt from lithium battery production. Cobalt is one of the most expensive components of LIBs. By reducing the amount of cobalt used in battery electrodes, manufacturers can lower the overall cost battery production making Portable Electronic Devices (PEDs) more affordable [20]. Additionally, cobalt is primarily mined at Democratic Republic of Congo where there is currently politically instability which can disrupt its supply. Quest for environmentally sound options may have also informed the introduction of non-harmful metals such as auminum in place of cobalt in PEDs lithium battery production.

Table 12: Previous results on metal concentration of LIBs and NiMH rechargeable batteries

Country	Battery Chemistry	Concentration (mg/kg)				
		Co	Li	Mn	Ni	References
Nigeria	NiMH	361284			75272	[18]
China	LIBs	50000 -200000	10000 - 30000		50000 -100000	[21]
UK and Germany	NiMH	55900	0	30200	432500	[14]
USA	LIBs	50000 -100000	50000 - 70000		50000 -200000	[16]
Singapore	Li-ion	220500	30300	4400	500	[6]
Singapore	Li-ion	160000	21000	700	400	[22]
Singapore	Li-ion	74400	51600	91000	159600	[6]
UK & Germany	Li-ion	207900	39700	18700	29900	[14]
China	Li-ion	156000	42000	205000	150000	[16]
Tehran	Li-ion	311800	70400	50200	90700	[19]
Present Study	NiMH	66287	13851	32899	82735	
Present Study	Li-ion	28899	65961	18310	24329	
Present Study	Li-polymer	29753	65477	21287	20159	

3.8 Environmental Implication and Potential Health Hazard

Improper disposal of waste rechargeable batteries can lead to the release of toxic chemicals and heavy metals into the air, soil and groundwater, posing great risk to plants, animals and humans when they spread through large areas, potentially entering the food chain leading diseases such as cancers, diseases of the central nervous system, kidney disorders, respiratory diseases, visual impairments, nausea, retarded cell growth, impairment of the reproductive system, cardiac arrest, etc. [23, 7]. Recycling, which helps to reduce the environmental pollution caused by the improper handling of these waste batteries has some demerits such as the emission of harmful gases from pyro metallurgy and the production of harmful waste during hydrometallurgy [15]. Rechargeable batteries can catch fire or explode if punctured or exposed to high temperatures. To mitigate these environmental implications and hazards, it’s essential to promote responsible consumption, proper disposal and recycling practices for rechargeable batteries such as battery collection programs, increasing public awareness about the environmental impacts of rechargeable batteries and the importance of recycling [18].

3.9 Estimation of Recoverable Metals from Waste Batteries

Data was mined from UN Comtrade Database [24] for the importation of batteries into Nigeria. This provided data on the quantities of rechargeable batteries imported into Nigeria from various countries (Table 13). It was assumed that at some points these batteries became waste and were disposed. Since the waste batteries contain valuable critical (scarce) raw materials, the study estimated the recoverable materials (metals) from the waste batteries. For a given year, the recoverable values were estimated using the relationship:

$$R_m = Q_b \times Mc \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad 1$$

Where R_m is the recoverable metal; Q_b is the quantity of battery imported; and Mc is the mean metal concentration (a given metal).

3.10 Estimation of Recoverable Metals

Presented in Table 13 are the recoverable metals (in metric tons) from the lithium batteries imported into Nigeria from 1999-2022.

Table 13: Recoverable Co, Li, Mn and Ni from batteries imported from 1999-2022

Year	Quantity of battery imported (tonnes)	Recoverable metals (t)			
		Co	Li	Mn	Ni
1999	179,308	5.2	11.8	3.3	4.4
2000	36,076	1.0	2.4	0.7	0.9
2001	42,259	1.2	2.8	0.8	1.0
2002	172,451	5.0	11.4	3.2	4.2
2006	69,760	2.0	4.6	1.3	1.7
2010	294,831	8.5	19.5	5.4	7.2
2015	1,835,634	53.0	121.2	33.6	44.6
Sum	2,630,319	75.9	173.7	48.3	64

Average concentration of the metals are: Co, 28.9 g/t; Li, 66 g/t; Mn, 18.3 g/t; and Ni, 24.3 g/t

3.11 Estimation of Recoverable Value from Recycling Waste Batteries

Presented in Table 14 is the estimate recoverable values (in Dollars) of the studied metals. It shows that lithium batteries imported into Nigeria from 1999-2022 had 75.9 tonnes of recoverable Co with an estimated recoverable value of $2.2 Million at a unit price of $28,550 [28]. Also, 173.7 tonnes of recoverable Li, which at a unit price of $15,343.30 [27] was estimated at a recoverable value of $2.7 Million. Furthermore, 48.3 tonnes of recoverable Mn, having a unit price of $1,690 [29] was estimated at a recoverable value of $81,347. In addition, 64 tonnes of recoverable Ni, at a unit price of $16,863 [30] was estimated at a recoverable value of $1.1 Million. Li had the highest recoverable value followed by Co, then Ni and Mn. The total recoverable value of the metals was $6 Million. From this, it can be deduced that a huge amount of money (foreign exchange) can be generated from the recycling of spent lithium batteries.

The recoverable values of the metals were calculated using their individual unit values in the international market which came up to $2.17 Million for cobalt, $2.7 Million for lithium, $0.08 Million for manganese and $1.08 Million for nickel; giving a total value of $6 Million for recoverable metals from imported lithium batteries between 1999-2022.

The percentage weight of battery in a mobile phone is estimated at 5.304 % [25]. 5.304 % of 82,100 tonnes [26] being the quantity of mobile phones imported gave 4351.3 tonnes as the quantity of battery in the mobile phones produced from1999-2022. Table 15 shows that 0.1 tonne of Co is recoverable from 4351.3 tonnes of the mobile phones imported from 1999-2022 which had a recoverable value of $3,590 at the mineral market. Also, 0.3 tonne of Li was estimated which had a recoverable value of $4,406. Mn was estimated at 0.08 tonne which had a recoverable value of $135 while Ni was estimated at 0.1 tonne and its recoverable value was $1,783. The total recoverable value of these metals was $9,914. This implies that a large sum of money can be recovered from recycling waste mobile phone batteries.

Table 14: Recoverable value of metals (in $) from lithium batteries imported into Nigeria from 1999 to 2022

Metal	Recoverable metal (t)	Unit price ($/t)*	Total value ($)
Cobalt	75.9	28550	2,170,258
Lithium	173.7	15343	2,663,609
Manganese	48.3	1690	81,347
Nickel	64	16863	1,077,343
Total Value			**5,992,557**

Table 15: Recoverable value of metals (in $) from mobile phones imported from 1999 to 2022

Quantity of battery (t)	Metal	Concentration (g/t)	Recoverable metal (t)	Unit price($/t)	Market value($)
4351.3	Co	28.9	0.1	28550	3,590
4351.3	Li	66	0.3	15343	4,406
4351.3	Mn	18.3	0.08	1690	135
4351.3	Ni	24.3	0.1	16863	1,783
Total value					**9,914**

The recoverable values of the individual metals came up as $3,590 for (Co), $4406 for Li, $135 for Mn and $1,783 for Ni which summed up to $9,914.

4. Conclusion and Recommendations

4.1 Conclusion

This study provides some insights into the metal levels of spent rechargeable batteries of portable electronics. The concentrations of Co, Li, Mn and Ni in Li-ion and NiMH batteries are so high and far above the TTLC, EPA and EU allowable limits for classifying these metals as toxic, some of which are 20, 40 or 100 percent beyond limits. As a result, spent batteries should be handled as toxic or hazardous wastes. Improperly handling of WRBs in Nigeria has the tendency of exposing residents and the entire ecosystem to health hazards. Recycling will make for resource conservation and generation of foreign exchange at the mineral market, thereby contributing to circular economy and economic growth. Extended Producer Responsibility (EPR) laws that hold electronics manufacturers responsible for the entire life cycle of their products including collection, recycling and disposal of electronic waste should be implemented. Advance Recycling Fee (ARF) can be introduced, in which case users pay for the end-of-life management of these batteries while purchasing the portable electronic devices. Products should be designed for durability, reparability and recyclability as well as promoting reuse to extend their lifespan. This helps to promote the principles of circular economy. Training programs and capacity-building procedures, recycling techniques and environmental regulations should be invested in.

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5.Supplementary Information (SI)

SI 1: Metal content of rechargeable batteries studied (mg/kg)

Sample ID	Co	Li	Mn	Ni
1	31390	60009	19781	23241
2	30981	74437	32549	35857
3	30303	64348	29230	31002
4	30778	55522	25739	7844
5	32737	71392	16897	34389
6	31054	71613	18241	34495
7	31114	57681	18944	27795
8	33397	81159	16864	32836
9	29104	72321	20843	12465
10	31814	65131	8461	12465
11	14207	52497	21793	6388
12	32386	47132	8821	3808
13	31693	70299	17012	33863
14	30591	71451	18628	34418

15	32498	64096	22722	11967
16	26869	63742	30260	30712
17	33555	71164	25575	15364
18	27947	70523	19228	33971
19	30085	61359	14518	29564
20	14076	55573	20954	7868
21	31005	71152	12707	4011
22	32650	73284	23312	2766
23	30872	65638	17309	31622
24	31696	69616	13845	14621
25	29010	67888	19178	32706
26	23348	59126	15583	28491
27	17743	55494	20506	26744
28	31593	64367	14501	31011
29	28237	67844	10851	32683
30	29010	67809	20388	32666
31	60993	15587	11192	80889
32	71581	12115	54605	84580
33	32616	76608	19813	7579
34	28955	65630	20627	31620

SI 2: Quantity of electrical electronic equipment imported from 1999-2022

EEE	Quantity imported (metric tonnes)
Cameras	280
Hot Water equipment	1437
Vacuum Cleaners	2536
Dishwashers	2761
Washing machines	5196
Food processing equipment	3118
Dryers	3744
Small Consumer Electronics	5068
Other Cooling	8011
Desktop PCs	8387
Household Heating & Ventilation	7,435
Microwaves	19,895
Household Tools	21,664
Professional IT	21,988
Flat display panel monitor	30,561

Laptop, notebooks and tablets	16,801
Small IT	35,707
Printers	53,795
Kitchen Equipment	67,707
Photovoltaic Panels	71,312
Mobile phones	82,100
Professional heating & ventilation	31,495
Other Small Household	105,573
CRT Monitors	160,114
Flat display panel TV	229,544
Household air conditioner	508,339
Fridge & Freezers	505,432
CRT TVs	2,558,043

Source: UN Comtrade Database (2023). United Nations Commodity Trade Statistics Database