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Heavy Metals Levels in Plastics Housing of Televisions: Is there a changing trend across three decades (1980-2000)?

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A B S T R A C T

Background:

This study investigated the concentration of some heavy metals in plastic housing of televisions produced over three decade (1980-2000) with the aim of providing information and comparing the trend in the concentration of these metals.

Methods:

The heavy metal concentrations were determined by atomic absorption spectroscopy after acid digestion using a 1:1 mixture of sulphuric and nitric acid.

Results:

The mean concentration of the heavy metals (mg/kg) in the television sets for 1980s, 1990s and 2000s, respectively, were as follows: 12.75 (Nd); 1.32 (Pb); 1.84, 1.47 & 2.79 (Ni); 1.53, 16.19 & 40.42 (Ag); 82.24, 159.69 & 113.29 (Zn); 7.12, 4.23 & 5.26 (Cr); 3.26, 2.76 & 2.39 (Cu); 4.84, 24.05 & 26.67 (V); 9.30, 8.40 & 12.63 (Co); 2.59, 4.05 & 4.28 (Cd).

Conclusion:

Although the mean concentrations for Zn, Cu and Ag in the television samples were relatively high, compared to the total threshold limit concentration (TTLC), they were below the threshold limit. These results suggest that there may not be any immediate environmental hazard posed from the TV plastic housings. The correlations analysis showed that most of the metals declined in TV housings over the subsequent decades.

Keywords:

Environmental Hazards, Heavy Metals, Plastics, Television, 1980's to 2000's Decades.

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INTRODUCTION

Electrical and electronic products, such as computers, mobile phones, television, digital recorders and many other household items continue to revolutionize social communication, entertainment, transportation, education and healthcare worldwide (1). There is no indication that this revolution will abate soon. Technical innovation will continue to be a cornerstone of social progress and advanced electronics are leading the way (2). Plastics have unique physical and electrical insulating properties, such as strength, resistance, flexibility, lack of electrical conduction. These properties are important for electronic devices, both for internal and external uses, especially in televisions and other household electronic devices.

Plastics have been the second largest components in Waste Electrical and Electronic Equipment (WEEE) and approximately 30 % of the mass electronic scrap consists of plastics (3,4). In Western Europe, plastic consumption by the industry was 2.78 million tons in 2002 and the quantity increased to 3.91 million tons, which is a rise of approximately 1.13 million tons for 2005 (5). Elements such as lead, cadmium, chromium, mercury, bromine, tin and antimony currently are or have been added to polymers as pigments, fillers, UV stabilizers and flame retardants. Typically, these materials do not chemically bind to plastic molecules but rather they create a suspension in the solid plastic polymer (6). Therefore, they may potentially dislodge from the plastic matrix over time. A visible symptom of such process is hazing on the surface of plastics caused by migration of bromine from the bulk of the material to the surface. This can create serious health problems and environmental hazards, as most of these elements are known to be toxic to humans.

Heavy metals are defined as elements with relatively high density compared to water molecule (7). Assuming that heavy molecular weight is associated with toxicity, heavy metals, including metalloids, (such as arsenic) are able to induce toxicity in humans even at trace amounts of exposure (8). Any metal (or metalloid) species may be considered a contaminant if it is unwanted or occurs in a form or concentration that

is detrimental to humans or environment (9). Metals/metalloids include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), vanadium (V), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants include aluminum (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U). These metals are significant environmental pollutants and their toxicity is a problem of increasing concern for ecological, nutritional, environmental and evolutionary reasons. Some of them; however, are essential for the body metabolism but they are toxic above their threshold levels. Ordinarily, they may enter the body in small amounts via respiration, ingestion, skin and drinking water. Some metals such as lead are not biologically significant in the body, and become toxic in the form of specific molecular complexes (9).

Television is primarily a mass medium for entertainment, education, news and advertising (10). People around the world are bombarded by advertising campaigns exhorting them to the latest, most fashionable models. As a result, television has become outdated and new models are introduced at a fast pace (11). The plastic in the television housing represents about 23 % of the total weight (12). Televisions contain a large number of heavy metals, which can pollute the air when burned or leached into the soil and drinking water, especially if buried in landfills.

The aim of this study was to determine the heavy metal levels in the plastic housing of select television models and find out if any changes in the levels have occurred over the three decades (1998-2000). Such an investigation is of significance, considering the large quantities of plastics being generated and the current concerns about the waste management practices.

MATERIALS AND METHOD

Sample Collection: Fifteen television sets manufactured between 1980 and 2000 were collected based on their availability. Five TVs from each of the 1980's, 1990's and 2000's were used in this study. These obsolete TV's of different brands were collected mainly from TV repair shops in Ogbete main market in Enugu and the computer village in Lagos, Nigeria. The TVs were complete but faulty and were kept in storage for possible recycling of the parts other than the plastic housing. The information on these TVs, such as brand and year of manufacture were obtained from the labels or from the retailers or repair shops. The TV brands used in this study were: President, Sharp, Grundig, Toshiba, Olevia, Goodness, Bush, Panasonic, Pacific, Tatung, Saisho, Philips, LG and Sharp.

Sample Preparation and Digestion: The plastic housings of the TVs were separated and crushed to pieces. The plastic samples were digested at 120^0C in a 1:1 ration mixture of H_2SO_4 (98 %): HNO_3 (70 %; 10 mL per 1g sample) and heated to near dryness. The digest was solubilized with 10mL deionized water, filtered and suspended in 100mL deionized water. Standard solutions of the suspended metals were prepared at two, four and six part per million (ppm) concentrations, and were aspirated into the burner to calibrate the atomic absorption spectrophotometer (AAS). The samples were analyzed for Pb, Ni, Ag, Zn, Cr, Cu, V, Co and Cd by the AAS equipped with an air/acetylene flame.

Validation Method: Glassware was properly washed and the reagents were of analytical grades (Riedel-de Haen, Germany). The accuracy of instrumental methods and analytical procedures were validated, using standard addition method. This was done by determining the metal concentrations in triplicate samples of un-spiked and spiked plastic housing samples. Spiking was performed by adding 1-3 mL of the metal standard solution (Table 1) to 1g of the sample, which was later subjected to the digestion procedure. The formula for calculating the percent recoveries was: % Recovery = $\frac{x-y}{z} \times 100$, where x was the concentration of spiked sample, y was the concentration of un-spiked sample; and z was the spiking concentration (mg/L). Sample blanks, prepared by taking 10mL of the mixture through the digestion procedure as the samples were analyzed for the metals. Table 1 shows the recoveries obtained via spiking of the samples with varying metal concentrations. Recoveries ranging from 92-96% were obtained. This validates the analytical procedure used.

Statistical Analysis: Spearman's coefficient correlation analysis was carried out to establish the presence of the heavy metals versus the plastic samples for the three decades. Analysis of variance was also performed with SPSS version 16 to determine and compare the significant difference ($p<0.05$) in the metals detected for each decade.

RESULTS

The mean concentrations of heavy metals in the plastic housing of TVs manufactured in the 1980's, 1990's and 2000's are shown in Tables 2, 3 and 4, respectively. Lead was detected in only three samples manufactured in 1980; however, it was not detected in any of the 1990's samples. Also, lead was detected in four out of the five samples manufactured in the 2000's. The mean concentrations of lead in the 1980's samples were much higher than the values obtained for 2000 samples. Silver was detected in only two 1980 samples while it was detected in all samples manufactured in the 1990's and 2000's. Much higher silver concentrations were detected in the 2000's samples compared to the other decades. Vanadium was detected in only one sample from the 1980's while it was detected in all samples for the 1990's and 2000's. Most of the other metals were detected in all of the samples across the three decades.

Table 5 represents the total mean concentrations of the heavy metals studied in the TV plastic housings for 1980's, 1990's and 2000's, and the TTLC values for the metals. The results were compared with the concentrations of heavy metals in electrical and electronic plastic material reported elsewhere and is presented in Table 6. Higher total mean concentrations of Ni, Ag, V, Co and Cd were detected in the samples

manufactured in 2000's while higher concentration of Pb and Cu were detected in the 1980's samples. The highest total mean concentration of Zn was documented for the 1990's samples. Table 7 presents the correlation analysis of the data. The analyzed data indicated that the concentration of heavy metals decreased as we progressed from 1980's to 2000's decades.

The analysis of variance (ANOVA) showed a significant difference ($p<0.05$) between each element in the sample manufactured within the same decade which was expected due to the limitation of not finding same product in the three decades. However, the Toshiba TV housing for the 1980's and 2000's showed an increase in the concentration of heavy metals.

Table 1. Percentage Recovery of heavy metals in the Television Plastic Housing.

Element	Spiking (added) conc.(mg/L)	Conc. of spiked sample (mg/L)	Conc. of unspiked sample (mg/L)	Recovered conc.	% Recovery
Mean ± S.D					**95%±0.01**
Pb	1.0000	0.9769	0.0769	0.9000	90
	2.0000	1.9587	0.0069	0.9759	98
	3.0000	2.9885	0.1111	0.9591	96
Mean ± S.D					**95%±0.04**
Ni	1.0000	0.9989	0.0080	0.9909	99
	2.0000	1.8670	0.0155	0.9258	93
	3.0000	2.8538	0.0425	0.9371	94
Mean±S.D					**95%±0.03**
Ag	1.0000	1.0002	0.0800	0.9202	92
	2.0000	1.9856	0.0662	0.9194	92
	3.0000	3.3002	0.5842	0.9053	91
Mean±S.D					**92%±0.58**
Zn	1.0000	1.5011	0.5116	0.9895	99
	2.0000	3.7758	1.8189	0.9785	98
	3.0000	3.9865	1.3244	0.8874	89
Mean±S.D					**95%±0.06**
Cr	1.0000	0.9924	0.1402	0.8522	85
	2.0000	2.0013	0.0410	0.9802	98
	3.0000	2.9937	0.1235	0.9567	96
Mean±S.D					**93%±0.07**
Cu	1.0000	1.0138	0.0202	0.9936	99
	2.0000	1.8341	0.0404	0.8969	90
	3.0000	2.9401	0.0580	0.9607	96
Mean±S.D					**95%±0.05**
V	1.0000	1.1263	0.1582	0.9621	96
	2.0000	2.1753	0.3733	0.9010	90
	3.0000	3.0183	0.1582	0.9534	95
Mean±S.D					**94%±0.03**
Co	1.0000	0.9871	0.0666	0.9205	92
	2.0000	2.1931	0.1982	0.9975	100
	3.0000	2.8813	0.0000	0.9604	96
Mean±S.D					**96%±0.04**
Cd	1.0000	1.0095	0.0703	0.9392	94
	2.0000	1.9672	0.0523	0.9575	96
	3.0000	2.8985	0.0111	0.9625	96

Table 2. Mean concentration ± standard deviation (mg /kg) of heavy metal in plastic housing of Television produced in the 1980's.

Heavy Metal	Television Brand				
	President	**Bush**	**Grundig**	**Toshiba**	**Panasonic**
Pb	9.44±1.87	42.80±10.02	11.53±2.27	Nd	Nd
Ni	Nd	1.76±0.32	2.09±0.71	3.72±2.54	1.63±1.48
Ag	2.32±4.02	Nd	Nd	5.33±4.62	Nd
Zn	50.56±4.02	37.99±2.99	84.85±12.27	166.77±37.04	71.04±7.46
Cr	3.36±3.04	25.67±6.67	Nd	2.73±2.37	3.81±3.81
Cu	4.70±0.84	3.92±0.95	2.93±0.72	1.84±0.76	2.91±0.16
V	24.20±10.32	Nd	Nd	Nd	Nd
Co	5.99±0.39	3.46±0.28	17.01±1.29	11.67±0.62	8.38±0.39
Cd	1.08±0.16	3.51±0.36	1.92±0.11	2.26±0.21	4.21±0.26

Nd = not detected

Table 3. Mean concentration ± standard deviation (mg /kg) of heavy metal in plastic housing of Television produced in the 1990's.

Heavy Metal	Television brand				
	Philips	**Goodness**	**Sharp**	**Saisho**	**Tatung**
Pb	Nd	Nd	Nd	Nd	Nd
Ni	1.49±1.49	Nd	1.06±0.38	3.47±3.13	1.34±1.05
Ag	69.16±32.91	2.62±4.54	4.16±3.88	4.98±4.31	0.09±0.04
Zn	205.09±9.01	213.25±30.48	134.59±7.84	168.55±19.99	76.96±6.93
Cr	3.34±3.08	3.39±3.12	5.94±5.90	4.49±3.99	3.98±3.98
Cu	2.37±0.73	3.67±0.60	4.18±0.52	2.28±0.70	1.31±1.13
V	12.03±20.84	28.61±11.42	23.88±20.68	23.72±10.20	31.99±5.10
Co	5.74±0.10	5.85±0.35	7.64±0.07	9.94±2.24	12.82±1.91
Cd	5.64±0.33	1.16±0.18	4.54±0.42	5.37±0.26	3.55±0.29

Nd = Not detected

Table 4. Mean concentration ± standard deviation (mg /kg) of heavy metal in plastic housing of Television produced in the 2000's.

Heavy Metal	Television brand				
	Pacific	LG	Sharp base	Olevia	Toshiba
Pb	5.41±1.11	0.38±0.33	0.43±0.19	Nd	0.39±0.16
Ni	1.62±0.33	1.70±1.54	2.29±2.07	1.19±0.39	7.15±7.53
Ag	46.59±25.12	57.69±34.48	4.93±4.27	48.75±42.22	44.14±47.78
Zn	138.89±31.94	50.17±1.46	102.51±12.79	56.13±6.45	218.73±37.83
Cr	5.52±1.8	12.81±0.81	Nd	3.16±2.91	4.81±1.24
Cu	1.44±0.47	3.83±3.25	3.14±0.59	1.68±0.69	1.83±0.75
V	22.92±19.85	24.14±20.90	39.41±27.54	11.37±19.70	35.50±5.62
Co	16.51±3.31	Nd	6.44±0.05	6.86±0.42	33.36±9.09
Cd	2.37±0.38	4.76±3.56	4.28±0.33	4.99±0.41	5.02±0.55

Nd = Not detected

Table 5. Total mean concentration of heavy metals (mg/kg) in the television plastic housing in the 1980's, 1990's and 2000's and the TTLC of the metals.

Heavy Metal	Mean ± S.D (Range), n = 5			TTLC (mg/kg)	N >TTLC
	1980	1990	2000		
Pb	12.75±17.61 (Nd-42.80)	0.00±0.00 (Nd)	1.32±2.29 (Nd-5.41)	1000	Nil
Ni	1.84±1.32 (Nd-3.72)	1.47±1.26 (Nd-3.47)	2.79±2.47 (1.62- 7.15)	2000	Nil
Ag	1.53±2.35 (Nd-5.33)	16.19±29.66 (0.09-69.16)	40.42±20.49 (4.93-57.69)	500	Nil
Zn	82.24±50.59 (37.99-166.77)	159.69±55.86 (76.96-213.25)	113.29±69.18 (50.17-218.73)	5000	Nil
Cr	7.12±10.48 (Nd-25.67)	4.23±1.07 (3.34-5.94)	5.26±4.73 (Nd-12.81)	2500	Nil
Cu	3.26±1.09 (1.84-4.70)	2.76±1.15 (1.31-4.17)	2.39±1.05 (1.44-3.83)	2500	Nil
V	4.84±10.82 (Nd-24.20)	24.05±7.55 (12.03-31.99)	26.67±11.12 (11.37-39.41)	2400	Nil
Co	9.30±5.27 (3.46-17.01)	8.40±3.00 (5.85-12.8)	12.63±12.99 (Nd-33.36)	8000	Nil
Cd	2.59±1.25 (1.08-4.21)	4.05±1.81 (1.16-5.64)	4.28±1.11 (2.37-5.03)	100	Nil

n = number of samples, N= number of samples above TTLC

Table 6. Heavy metal levels (mg/kg) reported in electrical and electronic plastic materials

Electrical & electronics device	Heavy Metals									References
	Pb	Cd	Ni	Zn	Cu	Cr	Ag	Co	V	
Plastic from electronic waste	17.41	5.71	-	360	570	8.38	-	-	-	(21)
Mobile phone	10140	2.93	9247	11007	203000	958	65.9	241.3	Nd	(22)
Cell phone	4667	Nd	1946	Nd	Nd	1470	235	145	Nd	(18)
TV plastic cabinet	295	6.7	-	75	392	-	-	-	-	(23)
Waste mobile phone plastic	58.3	69.9	432	-	-	-	403	-	-	(20)

Nd : not detected.

Table 7. Correlation across the three decades.

Metal	Decade	1980s	1990s	2000s
Pb	1980s	1.00		
	1990s	a	1.00	
	2000s	-0.672*	a	1.00
Ni	1980s	1.00		
	1990s	0.468	1.00	
	2000s	-0.159	-0.309	1.00
Ag	1980s	1.00		
	1990s	0.325	1.00	
	2000s	0.226	-0.022	1.00
Zn	1980s	1.00		
	1990s	-0.536*	1.00	
	2000s	-0.104	-0.571*	1.00
Cr	1980s	1.00		
	1990s	-0.685**	1.00	
	2000s	0.872**	-0.712**	1.00
Cu	1980s	1.00		
	1990s	0.262	1.00	
	2000s	-0.317	0.050	1.00
V	1980s	1.00		
	1990s	-0.684**	1.00	
	2000s	-0.346	-0.066	1.00
Co	1980s	1.00		
	1990s	0.500	1.00	
	2000s	0.092	0.496	1.00
Cd	1980s	1.00		
	1990s	-0.682**	1.00	
	2000s	0.514*	0.054	1.00

* Correlation was significant at the 0.05 level (2-tailed).
** Correlation was significant at the 0.01 level (2-tailed).
a Could not be computed because at least one of the variables is constant.

DISCUSSION

Based on the results, there is no particular trend in the concentrations of heavy metals in the plastic samples across the three decades. This might be in part due to differences in the manufacturing of the TV housings. Overall, we observed that the concentration of cadmium, silver and vanadium increased steadily across the three decades. While cadmium could have been incorporated as stabilizer and colorant in plastics, silver might have resulted from contamination with soldering materials in the TV housings. Specifically, replacing lead in soldering materials with bismuth, silver and copper may explain the presence of silver (13). Vanadium might also have originated from contamination during the manufacturing processes.

In general, the TV housings studied contained less than 50 mg/kg Pb, Ni, Cr, Cu, V, Co, and Cd. However, 98% and 7% of the samples contained more than 50mg/kg Zn and Ag, respectively. Also, the concentration of zinc was high across the studied decades, which was expected because zinc is used as a stabilizer, filler and colorant in plastics. Cobalt and chromium could have also been used as pigments, copper as biocides, lead and nickel as stabilizer or from the soldering materials in the TV industry. The solder compositions include Sn/Ag/Cu, Sn/Ag, and Sn/Bi/Ag alternatives. However, the Sn/Ag/Cu solders represent the preferred alternatives (14). Although these metals are useful, their negative effect on the environment and human health cannot be ignored, hence the need for monitoring their presence. These metals are potential environmental contaminants and can find their way into the foods, causing human health concerns. They are given special attention throughout the world due to their ubiquitous nature and toxic effects even at very low concentrations (15). Essentially, heavy metals have become a focus of public concern since analytical techniques have made it possible to detect them even at trace levels.

There have been governmental attempts to regulate these metal levels in plastics. The first attempt was introduced in mid 1990s by the European Community. The European Community "Packaging Directive" (EC Directive 94/62/EEC) has set the total amount of metals such as Cd, Cr, Hg, and Pb in plastic materials to be less than 100mg/kg (16, 17). Another European Union (EU) Directive (91/338/EC) sets the maximum allowable concentration of cadmium in plastics for consumer goods at 100mg/kg (18, 19). Similarly, the EU Directive on the Restriction of Hazardous Substances, RoHS (Directive 2002/95/EC), which became effective in July 2006, calls on manufacturers to be environmentally responsible and not use any homogenous material, parts or subassemblies that contains a maximum value of 0.1% by weight for Pb, Hg, Cr^{6+}, polybrominated biphenyls (PBB), polybrominated diphenyl ethers (PBDE), and 0.01% by weight in homogenous materials for Cd. The Total test is a chemical digestion procedure developed by the Department of Toxic Substances Control (20) to determine the total amount of a specific constituent in a sample material. This requires the chemical digestion of the sample to obtain the soluble and insoluble fractions. This analysis determines the total concentration of each target analyte in a sample. When any target analyte exceeds the toxicity threshold limit concentration (TTLC), the waste is classified as hazardous and the code is determined by the compounds that failed TTLC (16,18).

As presented in Table 5, the lead results were less than 1000 mg/kg; and cadmium and chromium concentrations were generally less than 100 mg/kg. These levels are the maximum allowable concentrations in homogenous components of electronic products by the Restriction of Hazardous Substances (RoHS) Directive. Although Zn, Cu and Ag were relatively high, all of them were below the TTLC. Hence, the plastic housing of the examined TVs do not constitute significant hazards; however, there is a need for their appropriate management and disposal. As seen in Table 6, the concentrations of heavy metals in the TV plastic housings were lower than those reported in previous studies (14, 20-23).

CONCLUSION

The results of this study showed that plastic housings of TVs manufactured between 1980 and 2000 contained varying amounts of heavy metals (lead, nickel, silver, zinc, chromium, copper, vanadium, cobalt and cadmium), which pollute the air when burned and leached into the soil and drinking water or if buried in landfills. Considering that the mean concentrations of the heavy metals were all below the levels set by the regulatory agencies, it can be deduced that the levels for TV plastic housings do not constitute a significant danger if managed appropriately. Therefore, policies guiding the disposal of electrical and electronic devices should be introduced to enhance their efficient and safe management.

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CONFLICT OF INTEREST

The authors declare no conflict of interest. *This paper was extracted from a M.Sc. thesis project conducted by Chioma Okenwa-ani submitted to the Department of Pure and Industrial Chemistry, University of Nigeria at Nsukka, Nigeria.*

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