



This work is licensed under
Creative Commons Attribution
4.0 International License.

DOI: 10.53704/fujnas.v10i2.364

A publication of College of Natural and Applied Sciences, Fountain University, Osogbo, Nigeria.

Journal homepage: www.fountainjournals.com

ISSN: 2354-337X(Online), 2350-1863(Print)

Essential Metals of Public Health Concern in Nigeria

^{1,2,3}Ajoke F. I. Apanpa-Qasim

¹The Council of Scientific and Industrial Research-National Environmental Engineering Research Institute Laboratory,
Nagpur – Maharashtra, India.

²Fountain University, Osogbo, Osun State

³Department of Chemistry, University of Ibadan, Ibadan - Nigeria

Abstract

Essential metals are imperative at every stage of human life. Their inclusion in consumer products has been seen over the years. Essential metals are used as fillers in paints. Fillers are granular solids incorporated to impart toughness and texture. The present study was conducted to evaluate the concentrations of essential metals from different manufacturers of paints with special emphasis on their health effects. Six metals, including Cr, Co, Ca, Ti, Mg and Al, were quantified using Inductively Coupled Plasma-Optical Emission Spectrometry. On comparative basis, fourteen paint manufacturers depicted the white paints had the highest concentrations of Ca (10,400.0 mg/kg), Ti (3,170.0 mg/kg) and Al (4,300.0 mg/kg) while green, chocolate and pink paints had the highest concentrations of Co (37.4 mg/kg), Mg (99, 510.0 mg/kg) and Cr (225.0 mg/kg), respectively. The highest concentrations were found in unregistered manufacturers except for Ti. Ti as a filler must have been used to thicken the film, support its structure and simply increase the volume of the paint. The problem of metals knowing what could be a safe exposure and recognising a hazardous exposure has been noted. While we could not make these judgments, it would be wise to adopt a precautionary approach and reduce human exposure to essential metals in paints to a practicable minimum. The toxicity of these metals can cause potential health hazards.

Keywords: *Essential metals; Fillers; Inductively Coupled Plasma-Optical Emission Spectrometry; Paint Manufacturers*

Introduction

The architectural coating segment dominates the world paint and coatings market (Koncept Analytics, 2014). Apart from the construction and automotive sectors, other end-use industries relying on the paints and coatings sector include marine, wooden furniture, and steel. Manufacturers' application of different paint types for decoration and aesthetics is as old as human civilisation (Frost and Sullivan, 2014).

Interestingly, the production of chemicals worldwide has increased dramatically in recent years. The global market for chemicals has shown a 10-fold increase worldwide (WHO, 2010). With recent construction and metal technology advances, increased environmental contamination has contributed to severe health effects (Manisalidis et al., 2020). Worrisome enough is the production of

Corresponding author ORCID iD: 0000-0002-0559-8131

Email address: ajoketola@gmail.com

chemicals in many developing countries where public health laws are either weak or insufficient to protect the health of their workers and residents

Importance of decoration and maintenance is a priority to most homeowners using water-based paints. Paints are composed of different organic and inorganic materials: pigment, filler, binder, and additives. Fillers are a particular type of pigment that serves to thicken the film, support its structure and increase the volume of the paint (Haseeb Jamal, 2017). They are known as extenders. They are usually cheap and inert materials, such as diatomaceous earth, talc, lime, barytes, clay. Floor paints that must resist abrasion may contain fine quartz as fillers. Examples of fillers are calcium carbonate, talc, silica or quartz, alumina hydrate, mica, and pumice (Tony Johansen, 2006, Talbert, 2007).

Essential metals are considered 'safe' with few if any significant implications for human health (Engwa et al., 2019; Ugonna et al., 2020). Metals undoubtedly account for significant mortality and morbidity due to environmental exposure and improper management of selected chemicals (Manisalidis et al., 2020). Toxicity can result from metals such as lead, arsenic, cadmium, iron, zinc, and chromium (Jaishankar et al., 2014; Jyothi, 2020).

Micro-nutrients are a vital dietary supplement, although only small amounts of metals are needed for well-being (Gombart et al., 2020; Upadhaya and Kim, 2020). Increased exposure to the metals may result in health problems including skin allergies, severe redness, swelling/skin ulcers, cellular death, DNA damage, oxidative stress, neurotoxicity, carcinogenicity, mental disorder, and reproductive failure health effects (Anyanwu et al., 2018).

The present study focused on determining essential metal concentrations in selected paint products and appraising health effects in this context. It is anticipated that the present study will provide pivotal information about the usage of essential metals as fillers likely to pose health risks (Briffa et al., 2020).

Materials and Methods

Sample Collection and Metal Determination

Popular paint markets in Ibadan and Lagos were selected for sample purchase and collection. Over one hundred and fifty (>150) paint samples were collected from 14 different manufacturers. Samples collected were stored in air-tight plastic containers. Metal analysis in samples was carried out at the Council of Scientific and Industrial Research- National Environmental Engineering Research Institute Laboratory, Nagpur – Maharashtra, India.

5.0 g of paint sample was spread on glass slides using different brushes for all samples. The glass slides were dried in an oven at 120 °C for 2 hrs. Dried paint chips of 1.0 g were weighed into closed Teflon vessels and subsequently digested in a closed microwave digestion system using 10 mL of 70 % nitric acid and 3 mL of 98 % sulphuric acid. After digestion, the samples were cooled to room temperature and were filtered using 90mm filter paper grade 393 by Sartorius, Germany, and the final volume (50 mL) was adjusted by deionised water. The deionised water used in the analysis had an electrical resistivity of 10 MΩ/cm. Blanks were also prepared following the same procedure with each batch of samples (n = 10). Obtained filtrates were analysed using Thermo Scientific iCAP 6300 Duo Inductively Coupled Plasma-Optical Emission Spectrometry. Working standard solutions of 1-1000 ppm were prepared from multi-element standards. The reference materials (commercial standards) used were from CPA Chem. Ltd., Bulgaria. Calibration with a linear regression value (R^2) of 0.999 was established for each element. Sample blanks were prepared, and dilutions were done when necessary. Countercheck of the results was ensured through the standard internal analysis and standard reference materials, which showed an excellent recovery (80-110%).

Instrument Operation Conditions

The instrument operating conditions in the analysis of metals is shown in Table 1.

Table 1: Operating conditions of instruments used for the analysis of paint samples

Operating condition	Microwave digester	ICP-OES
Carrier gas		Ultra-pure Argon
Gas flow rate		-
Injection temperature		-
Detector temperature		-
column temperature		-
	Instrument temperature: 210 °C	RF power: 1150 W
	Operating power: 1000 watt	Plasma flow: 0.5 litres/ min
	ramp time: 25mins	Pump rate: 50 rpm
	holding time: 30mins at 200 °C	Auxiliary gas flow: 0.5 L/min
		Nebulizer gas flow: 0.5 L/min

Results and Discussion

The Concentration of Metals in Paint Samples Concerning Manufacturers

Fourteen selected manufacturers of paints: six registered with NIS- Nigerian Industrial Standard, ISO – International Organization for Standardization; and eight unregistered manufacturers that produced different paints were studied as seen in Table 2. The mean \pm SD of Ca, Mg, Al, Cr, Co, Ti for manufacturers in the paint samples collected in Lagos and Ibadan, Nigeria, is presented in Table 3. Figure 1 shows variation in metals concentration observed.

Calcium

The concentrations of calcium in all the 174 paint samples with respect to manufacturers ranged from 614-10,400 mg/kg in products by manufacturers C and N, respectively. The highest concentration of Ca was 10,400 mg/kg obtained in paints produced by manufacturer N, an unregistered manufacturer and was followed by 10,300 mg/kg and 9,980 mg/kg in the same products produced by manufacturer N. The highest mean concentration of Ca was $9,839.2 \pm 68.6$ mg/kg obtained in paint produced by manufacturer N. This was followed by $9,328.7 \pm 60.2$ mg/kg and $7,696.3 \pm 48.0$ mg/kg in

paint produced by different manufacturers such as manufacturer I and J while the lowest concentration was 723.7 ± 9.1 mg/kg in paints produced by manufacturer C. The permissible limit of calcium recommended by WHO in drinking water is 75 mg/L (Kumar and Puri, 2012). Calcium is used as filler, and it has no available limit in paints.

Calcium is one of the most ubiquitous metal ions in cellular systems controlling almost all life processes such as triggering life at fertilisation and developing and differentiation of cells into specialised types (Williams, 2007). Calcium is also one of the most versatile and universal signalling agents in the human body. It acts as an intracellular messenger, relaying information within cells to regulate their activity (Kazmierczak et al., 2013). It has been proven that very high concentrations of Ca^{2+} can lead to the disintegration of cells and that this process is controlled through the activity of Ca^{2+} sensitive protein-digesting enzymes. Calcium is also involved in programmed cell death, known as apoptosis. The Ca^{2+} signalling mechanism, which triggers a new life at fertilisation and is then re-used to regulate the developmental program, is suddenly transformed from a signal of life to death (Berridge *et al.*, 1998).

Table 2: Information on paint samples collected from Lagos and Ibadan, Nigeria.

Serial No.	Manufacturer code	Number of different paint colours collected	Number of paint samples collected	NIS-ISO registration
1	A	10	20	Yes
2	B	9	18	Yes
3	C	9	18	Yes
4	D	5	10	Yes
5	E	5	10	Yes
6	F	6	12	Yes
7	G	4	8	No
8	H	5	10	No
9	I	4	8	No
10	J	5	10	No
11	K	6	12	No
12	L	8	16	No
13	M	7	14	No
14	N	4	8	No

Note: The number of paint colours collected per manufacturer was most commonly patronised based on availability.

Table 3: Mean concentrations (dry weight, mg/kg) of metals in paint samples in respect to manufacturers

Serial No.	Manufacturers	Ca	Al	Co	Cr	Mg	Ti
1	A	3613.4±168.7	3207.4±105.5	14.6±0.3	12.0±1.4	83079.5±1515.1	2599.3±90.2
2	B	3519.2±74.3	2763.7±39.7	16.4±0.8	14.6±0.9	82704.8±814.5	1153.3±40.2
3	C	723.7±9.1	1482.1±37.4	6.3±0.2	16.7±1.3	4730.7±246.6	2586.1±78.6
4	D	1902.2±32.3	1713.2±69.6	13.8±0.2	15.9±1.3	30755.1±592.8	1515.5±23.1
5	E	1734.4±27.5	1536.4±8.3	17.0±0.3	16.3±0.4	33199.2±455.1	1776.2±19.3
6	F	1905.6±27.7	1684.0±48.8	16.0±0.3	16.1±1.4	22878.8±975.4	1819.2±62.2
7	G	6015.0±44.8	2529.0±15.2	15.2±0.1	163.1±36.2	81771.8±1202.8	1736.4±38.7
8	H	6345.6±71.0	2819.5±66.7	18.7±0.6	65.2±2.2	81699.0±601.8	1285.8±26.8
9	I	9328.7±60.2	3112.7±13.6	29.5±0.7	130.1±1.9	92147.9±632.3	1487.7±15.1
10	J	7696.3±48.0	3186.0±27.8	29.2±0.7	43.7±0.6	80666.2±593.5	1522.0±28.6
11	K	5062.4±40.4	2479.3±37.6	17.7±0.8	25.5±1.5	26257.2±1185.1	1574.4±60.6
12	L	6706.7±55.3	2487.2±26.5	28.0±1.1	38.1±2.2	84219.8±3821.5	1417.7±41.4
13	M	622.63±44.6	2764.7±64.5	27.9±0.3	35.2±0.7	37736.2±1205.0	1486.9±34.9
14	N	9839.2±68.6	2770.1±10.2	35.6±0.5	110.7±8.2	78496.1±1347.2	1441.1±103.4

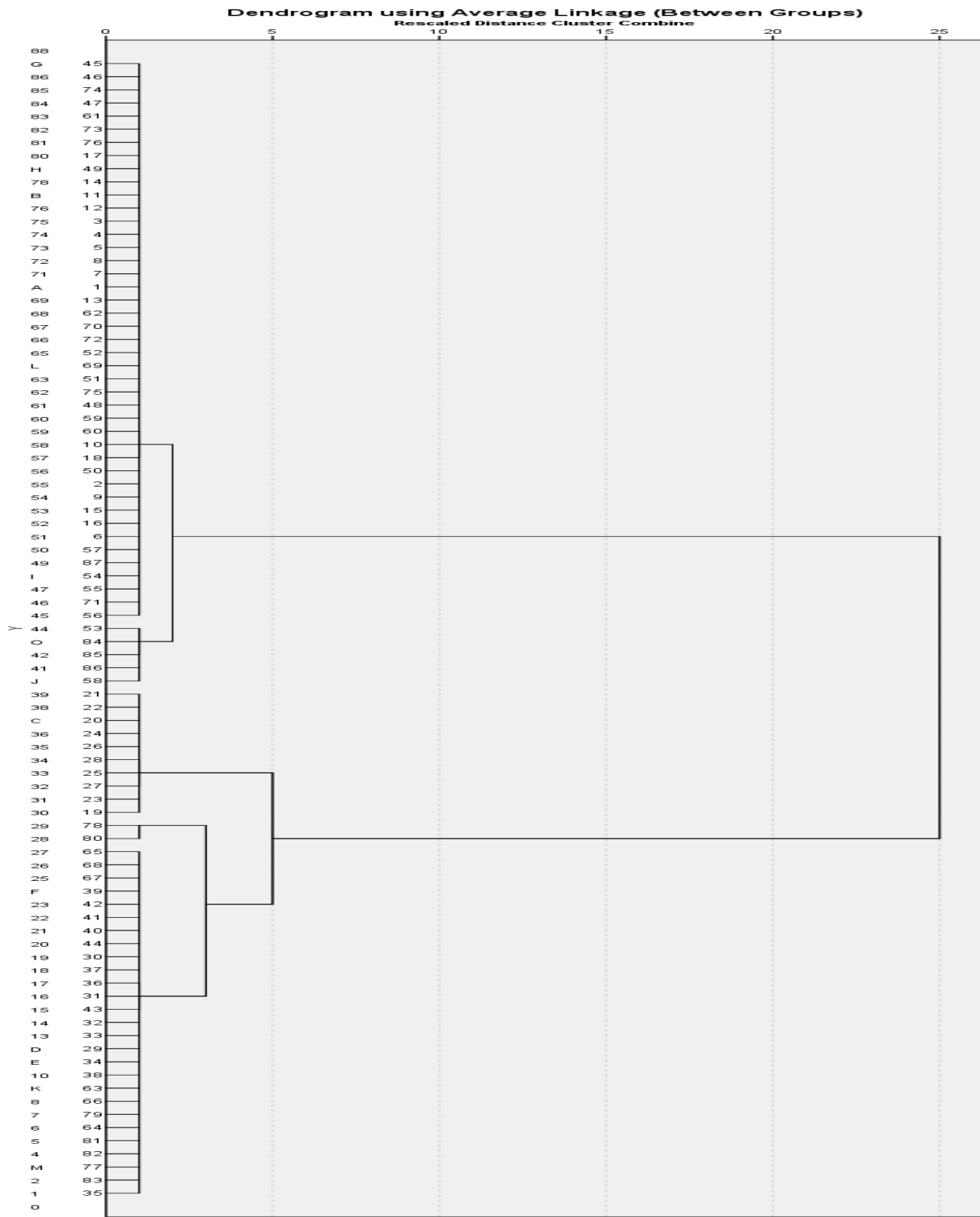


Figure 1: A hierarchical cluster analysis dendrogram with respect to manufacturers

Magnesium (Mg)

The magnesium concentrations in the paint samples with respect to manufacturers ranged from 4,000-99,510 mg/kg in products by manufacturers C and L, respectively. The highest concentration of Mg was 99,510 mg/kg obtained in paints produced by manufacturer L, an unregistered manufacturer and followed by 95,300 mg/kg and 94,900 mg/kg in products produced by paint manufacturers I and N (unregistered manufacturers). The highest mean concentration of Mg was $92,147.9 \pm 632.3$ mg/kg obtained in paints produced by paint manufacturer I and followed by $84,219.8 \pm 3,821.5$ mg/kg and $83,079.5 \pm 1,515.1$ mg/kg in paint produced by manufacturer L and A, respectively, while the lowest concentration was $4,730.7 \pm 246.6$ mg/kg in paints produced by manufacturer C. There is no permissible limit of Mg in paints. The permissible limit of magnesium recommended by WHO in drinking water is 50 mg/L (Kumar and Puri, 2012).

Magnesium is one element that supports life; many studies have been performed regarding physiological functions and correlation with diseases. Magnesium has many different purposes and may end up in the water differently. Chemical industries add magnesium to plastics and other materials as a fire protection measure or filler (Karakas *et al.*, 2011).

Aluminium (Al)

The concentrations of aluminium in the paint samples with respect to manufacturers ranged from 1,090-4,300 mg/kg in products by manufacturers E and J, respectively. The highest concentration of Al was 4,300 mg/kg obtained in paints produced by manufacturer J, an unregistered manufacturer, followed by 4,170 mg/kg and 3,720 mg/kg in products produced by paint manufacturers J I (unregistered manufacturers). The highest mean concentration of Al was $3,207.4 \pm 105.5$ mg/kg obtained in paint produced by manufacturer A and was followed by $3,186.0 \pm 27.8$ mg/kg and $3,112.7 \pm 13.6$ mg/kg in paint produced by manufacturer J and I, respectively, while the lowest concentration was $1,482.1 \pm 37.4$ mg/kg in paints produced by manufacturer C. There is no available limit of Al in paints. The amount of aluminium present in drinking water has been recommended to

be below 200 $\mu\text{g/L}$ by the World Health Organization (WHO, 2006).

The ability to separate aluminium metal from its ores on an industrial scale changed aluminium from a primarily decorative metal to the most widely used metal of the 21st century. Aluminium's success as a modern material with myriad applications comes from a wide breadth of physical and chemical properties that, combined with its ubiquity in nature, make it an extremely cost-effective natural resource that has found a promising application in the paint industry. The cause of Alzheimer's disease is still unknown, but aluminium might play a significant role in its cause (Al Zubaidyl *et al.*, 2011). Medical researches link aluminium to the various brain, blood, bones diseases and breast cancer (Al Zubaidyl *et al.*, 2011; Sappino *et al.*, 2012). The largest source of aluminium comes from municipal water supplies. Many municipal water supplies are treated with both aluminium sulphate and aluminium fluoride. Groundwater can also be contaminated through industrial activities such as paint production.

Titanium (Ti)

The concentrations of titanium in the paint samples with respect to manufacturers ranged from 1,010-3,170 mg/kg in products by manufacturers H and A, respectively. The highest concentration of Ti was 3,170 mg/kg obtained in paints produced by manufacturer A, a registered manufacturer, followed by 3,080 mg/kg and 3,060 mg/kg in the same product produced by manufacturer A. The highest mean concentration of Ti was $2,599.3 \pm 90.2$ mg/kg obtained in paint produced by manufacturer A and was followed by $2,586.1 \pm 78.6$ mg/kg and $1,819.2 \pm 62.2$ mg/kg in paint produced by manufacturer C and F, respectively, while the lowest concentration was $1,153.3 \pm 40.2$ mg/kg in paints produced by manufacturer B. WHO does not set the permissible limit of titanium in the paints or the environment. The International Agency for Research on Cancer (IARC), therefore, has classified TiO_2 as a Group 2B carcinogen (possibly carcinogenic to humans) (IARC, 2006; Valko *et al.*, 2006). Pulmonary inflammatory responses and lung cancers are the most important adverse effect

observed in experimental animals due to TiO₂ nanoparticles exposures (Xu et al., 2013).

Chromium (Cr)

The concentrations of chromium in the paint samples with respect to manufacturers ranged from 10.3-225 mg/kg in the same product by manufacturer G. The highest concentration of Cr was 225 mg/kg obtained in paints produced by manufacturer G, an unregistered manufacturer. It was followed by 205 mg/kg and 201 mg/kg in the same product by manufacturer G. The highest mean concentration of Cr was 163.1±36.2 mg/kg obtained in paint produced by manufacturer G. This was followed by 130.1±1.9 mg/kg and 110.7±8.2 mg/kg produced by manufacturers G and N, respectively. In contrast, the lowest concentration was 12.0±1.4 mg/kg in paint produced by manufacturer A.

The permissible limit of chromium in paints is set at 60 mg/kg (EU REACH EN 71-3, 2009). Paint samples produced by manufacturers G, I and N (unregistered manufacturers). According to US EPA, 0.1 mg/L for total chromium, which includes all forms of chromium including Cr (VI), is permissible in drinking water (USEPA, 2010). The permissible limit of chromium recommended by WHO in plants is 1.30 mg/kg (Nazir et al., 2015), and in the soil is 100 mg/kg (Chiroma et al., 2014).

Chromium is an essential trace element for living organisms. However, a slight elevation in the level of Cr⁶⁺ elicits environmental and health problems because of its high toxicity, mutagenicity and carcinogenicity (Nath et al., 2008). In the environment, Cr⁶⁺ contamination alters the structure of soil microbial communities (Gürkan et al., 2012).

The United States Environmental Protection Agency (US EPA) has identified Cr⁶⁺ as one of the 17 chemicals posing the greatest threat to humans (Agrawal, 2012). Cr (VI) is also toxic to many plants, aquatic animals, and microorganisms (Velma et al., 2009; Vemula et al., 2013). Chromium is extensively used in metallurgy, electroplating, production of paints and pigments, tanning, wood preservation, chemical production and pulp and paper production.

Cobalt (Co)

The concentrations of cobalt in the paint samples with respect to manufacturers ranged from 4.3-37.4 mg/kg in the same product by manufacturer N. The highest concentration of Co was 37.4 mg/kg obtained in paints produced by manufacturer N, an unregistered manufacturer. It was followed by 36.9 mg/kg, and 36.7 mg/kg in the same product by manufacturer N. The highest mean concentration of Co was 35.6±0.5 mg/kg obtained in paint produced by manufacturer N. This was followed by 29.5±0.7 mg/kg and 29.2±0.7 mg/kg products produced by paint manufacturers I and J, respectively while the lowest concentration was 6.3±0.2 mg/kg in paint produced by manufacturer C. The permissible limit of cobalt recommended by WHO in the soil is 50 mg/kg (Chiroma et al., 2014), in drinking water is 1–2 ppb (ATSDR, 2004a). The international organisation responsible for setting standard levels of vitamin intake, the FAO (Food and Agricultural Organization of the United Nations) and WHO (World Health Organization), recommend a 2.4 µg/day of vitamin B₁₂ (equivalent to 0.1 µg/day of vitamin B₁₂).

Cobalt is the form of Vitamin B₁₂ that is essential for humans. Vitamin B₁₂ supports important synthetic reactions in metabolic processes and is essential for producing red blood cells and required for reproductive health. Human exposure can cause heart disease lung cancer through inhalation.

Concentration of Metals in Paint Samples with respect to Colours

The concentrations of metals with respect to colours by the different manufacturers are shown in Table 4.

Calcium

The calcium concentrations in the paint samples with respect to colours ranged from 614-10,400 mg/kg in chocolate and white paint. The highest concentration of Ca was 10,400 mg/kg in white paint, followed by 10,300 mg/kg and 9,980 mg/kg in white and cream paint, respectively. The highest mean concentration of Ca with respect to colours was 5,866.4±30.7 mg/kg in white paint, followed by 5,246.4±66.7 in cream and 5,160±90 mg/kg in

Table 4: Mean concentrations (dry weight, mg/kg) of metals in paint samples with respect to colours

	Al	Ca	Cr	Co	Mg	Ti
BLUE	2391.0±38.5	4880.6±61.0	52.3±1.9	20.5±0.5	57130.5±2423.9	1729.9±75.9
BROWN	2377.8±80.5	3504.2±171.7	18.2±0.4	15.9±0.2	65758.6±1260.7	2057.4±82.1
CHOCOLATE	2364.8±17.0	3920.3±60.1	23.1±0.6	16.6±1.1	52140.7±5372.6	2013.7±15.3
CREAM	2472.9±57.7	5246.4±66.7	54.0±20.9	21.1±0.9	64043.6±1641.7	1595.0±58.4
GREEN	2380.4±61.1	4853.4±85.4	47.4±5.7	20.6±0.5	56996.2±797.2	1614.9±41.4
GREY	2263.6±69.7	2244.8±285.1	13.6±0.2	10.1±0.2	45984.5±2395.6	2544.2±36.1
ORANGE	2649.3±44.7	5028.0±73.4	29.2±2.2	23.0±1.0	69688.6±1458.0	1323.1±43.1
PINK	2777.2±46.4	5155.1±89.7	35.3±1.3	21.7±0.5	72266.9±2727.5	1553.6±74.5
RED	2428.6±21.7	3614.6±56.9	24.0±1.6	18.0±0.4	44145.9±1473.5	1743.9±68.4
VIOLET	1441.5±50.1	708.6±7.4	13.6±4.2	5.4±0.2	4273.7±393.5	2578.3±125.0
WHITE	2752.8±88.4	5866.4±30.7	49.1±1.7	20.6±0.6	59720.7±1069.1	1712.4±60.0
YELLOW	2150.5±6.4	2278.5±50.4	15.4±0.6	14.4±0.3	46771.9±1719.3	1948.4±25.4

pink paint. The lowest concentration, 708.6±7.4 mg/kg, was obtained in violet paint.

Magnesium

The magnesium concentrations in the paint samples for colours ranged from 4,000-99,510 mg/kg in violet and chocolate paint. The highest concentration of Mg was 99,510 mg/kg in chocolate paint, followed by 95,300 mg/kg and 94,900 mg/kg in white paints. The highest mean concentration of Mg for colours was 72,266.9±2,727.5 mg/kg in pink paint, followed by 69,688.6±1,458.0 mg/kg in an orange and 65,758.6±1,260.7 in brown paint. The lowest concentration, 4,273.7±393.5 mg/kg was obtained in violet paint.

Aluminium

The aluminium concentrations in the paint samples with respect to colours ranged from 1,090-4,300 mg/kg in blue and white paint. The highest concentration of Al was 4,300 mg/kg in white paint, followed by 4170 mg/kg and 3,720 mg/kg in other white paints. The highest mean concentration of Al with respect to colours was 2,777.2±46.4 mg/kg in pink paint, followed by 2,752.8±88.4 mg/kg in pink and 2,649.3±44.7 mg/kg in orange paint. The

lowest concentration, 1,440±50 mg/kg was obtained in violet paint.

Chromium

The chromium concentrations in the paint samples with respect to colours ranged from 10.3-225 mg/kg in cream and pink paint. The highest concentration of Cr was 225 mg/kg in pink paint, followed by 205 mg/kg in blue and 201 mg/kg in blue paint. The highest mean concentration of Cr with respect to colours was 54.0±20.9 mg/kg in cream paint, followed by 52.3±1.9 mg/kg in blue and 49.1±1.7 mg/kg in white paint. The lowest concentration, 13.6±0.2 mg/kg, was obtained in grey paint.

Cobalt

The concentrations of cobalt in the paint samples with respect to colours ranged from 4.3-37.4 mg/kg in brown and green paint. The highest concentration of Co was 37.4 mg/kg in green paint, followed by 36.9 mg/kg in white and 36.7 mg/kg in blue paint. The highest mean concentration of Co with respect to colours was 23.0±1.0 mg/kg in orange paint, followed by 21.7±0.5 mg/kg in pink and 21.1±0.9 mg/kg in cream paint. The lowest concentration, 5.4±0.2 mg/kg, was obtained in violet paint.

Titanium

The concentrations of titanium in the paint samples with respect to colours ranged from 1,010-3,170 mg/kg in blue and white paint. The highest concentration of Ti was 3,710 mg/kg in white paint, followed by 3,080 mg/kg and 3,060 mg/kg in brown paints. The highest mean concentration of Ti with respect to colours was $2,578.3 \pm 125.0$ mg/kg in violet paint, followed by $2,544.2 \pm 36.1$ mg/kg in grey and $2,057.4 \pm 82.1$ in brown paint. The lowest concentration, $1,323.1 \pm 43.1$ mg/kg, was obtained in orange paint.

The order of metal concentrations in the paint samples with respect to colour was Ca: white > cream > pink > orange > blue > green > chocolate > red > brown > yellow > grey > violet; Mg: pink > orange > brown > cream > white > blue > green > chocolate > yellow > grey > red > violet; Al: pink > white > orange > cream > red > blue > green > brown > chocolate > grey > yellow > violet; Cr: cream > blue > white > green > pink > orange > red > chocolate > brown > yellow > grey > violet; Co: orange > pink > cream > green > white > blue > red > chocolate > brown > yellow > grey > violet; Ti: violet > grey > brown > chocolate > yellow > red > blue > white > green > cream > pink > orange.

Cluster Analysis

Results revealed three clusters of the six examined metals: The dendrogram identified data groups with respect to manufacturers as shown in Figure 1 and 2 with Cases 1-18, 45-62, 69-76; 84-87; Cases 2: 19-28; Cases: 29-44; 63-68; 77-83. It was observed that the dendrogram in the data groups with respect to colours was the same as that of manufacturers. As seen in Cases 2: 19-28, the grouping with respect to colours and manufacturers was specific for manufacturer C, a registered manufacturer.

Conclusion

The present study demonstrated wide variations

in the concentrations among metals in water-based paints, determined mainly by the pigments and fillers used. The highest concentration of the metals shows Cr was 225 mg/kg from G (an unregistered manufacturer) in pink coloured paint, and Co was 37.4 mg/kg from N (an unregistered manufacturer) in green coloured paint. Of the essential heavy metals, the highest concentrations of Ca (10,400 mg/kg) from N (an unregistered manufacturer) in white coloured paint, Ti (3,170 mg/kg) from A (registered manufacturer) in white coloured paint, Mg (99,510 mg/kg) from L (an unregistered manufacturer) in chocolate coloured paint and Al (4,300 mg/kg) from J (an unregistered manufacturer) in white coloured paint. Metals usually used as fillers (Al, Ti, Mg, Ca) had high levels compared to pigment metals (Co, Cr), while the unregistered manufacturers had excessive levels of metals compared to registered manufacturers.

Effective legislation, guidelines and market check of paint samples are necessary. Failure to control the exposure will result in severe complications in the future because of the adverse effects imposed by these metals. National, as well as international co-operation, is vital for framing appropriate tactics to prevent metal toxicity.

Lastly, efforts need to be undertaken to assess high metal levels in existing houses (scraps) of these metals in decorative water-based paint to reduce indoor pollution.

Acknowledgement

Part funding of this research work (FR number: 3240275040) was sponsored by The World Academy of Sciences for the Advancement of Science in developing countries and the Council of Scientific and Industrial Research, Nagpur, India.

Conflict of interest statement: None

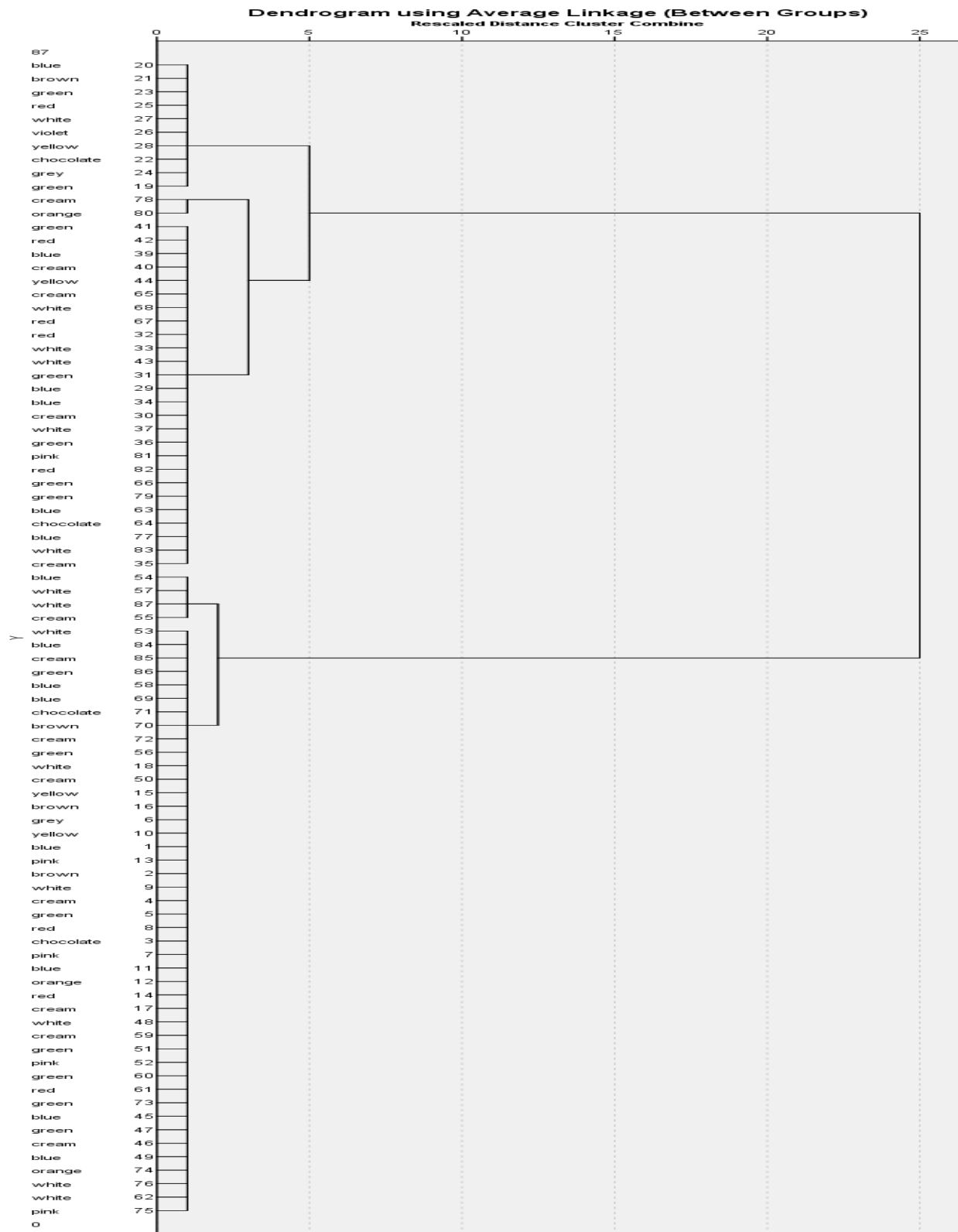


Figure 2: A hierarchical cluster analysis dendrogram with respect to colours

References

- Agency for Toxic Substances and Disease Registry (ATSDR). (2004a). Toxicological profile for cobalt. Atlanta, GA: US Department of Health and Human Services, Public Health Service. Retrieved Nov.11, 2021, from <http://www.atsdr.cdc.gov/toxprofiles/TP.asp?id=373&tid=64>.
- Agrawal A. (2012). Toxicity and fate of heavy metals with particular reference to developing foetus. *Advanced Life Sciences*; 2 (2): 29-38.
- Al Zubaidy, E. A., Mohammad, F. S. and Bassioni, G. (2011). Effect of pH, salinity and temperature on aluminium cookware leaching during food preparation. *International Journal of Electrochemical Science* 6 (12): 6424-6441.
- Anyanwu, Brilliance O., Anthonet N. Ezeji for, Zelinjo N. Igweze, and Orish E. Orisakwe (2018). "Heavy Metal Mixture Exposure and Effects in Developing Nations: An Update" *Toxics* 6, no. 4: 65. <https://doi.org/10.3390/toxics6040065>
- Apanpa-Qasim, A.F.I., A.A. Adeyi, M.N. Mudliar, K. Raghunathan & P. Thawale. (2016). Examination of Lead and Cadmium in water-based paints Marketed in Nigeria. *Journal of Health and Pollution*. 6: 43-49.
- Berridge, M.J.; Bootman, M.D.; Lipp, P. (1998). Calcium—a life and death signal. *Nature*, 395, 645-648.
- Briffa, J., Sinagra, E., Blundell., R (2020). Heavy metal pollution in the environment and their toxicological effects on humans. Volume 6, Issue 9, September 2020, e04691. <https://doi.org/10.1016/j.heliyon.2020.e04691>
- Chiroma, T.M., R.O. Ebewe, and F.K. Hymore. (2014). Comparative assessment of heavy metal levels in soil, vegetables and urban grey wastewater used for irrigation in Yola and Kano. *International Refereed Journal of Engineering and Science*. 3: 01-09.
- European Union Eco label (EU Ecolabel) criteria for 'Outdoor Paints and Varnishes' and 'Indoor Paints and Varnishes'. (2010). Adopted August 2010 (2009/543/EC2 and 2009/544/EC3) Wall paints – UZ17 and UZ01.
- Frost and Sullivan. (2014). Analysis of the industrial paints and Coatings Market in South Africa, Nigeria and Kenya. Retrieved Nov. 11, 2021. <http://www.reportlinker.com/p02148671/Analysis-of-the-Industrial-Paints-and-Coatings-Market-in-South-Africa-Nigeria-and-Kenya.html>.
- Godwill A. E., Paschaline U. F., Friday N.N. & Marian N. U. (2019). Mechanism and Health Effects of Heavy Metal Toxicity in Humans, Poisoning in the Modern World - New Tricks for an Old Dog?, Ozgur Karcioglu and Banu Arslan, IntechOpen, DOI: 10.5772/intechopen.82511. Available from: <https://www.intechopen.com/chapters/64762>
- Gombart, A. F., Pierre, A., & Maggini, S. (2020). A Review of Micronutrients and the Immune System-Working in Harmony to Reduce the Risk of Infection. *Nutrients*, 12(1), 236. <https://doi.org/10.3390/nu12010236>
- Gürkan, R., H.I. Ulusoy, M, & Akçay M. (2012). Simultaneous determination of dissolved inorganic chromium species in wastewater/natural waters by surfactant sensitised catalytic kinetic spectrophotometry. *Arabian Journal of Chemistry*. 2012. [in press].
- International Agency for Research on Cancer (IARC). (2006). Cobalt in Hard Metals and Cobalt Sulfate, Gallium Arsenide, Indium Phosphide and Vanadium Pentoxide. IARC Scientific Publication, 86
- Jaishankar, M., Tseten, T., Anbalagan, N., Mathew, B. B., & Beeregowda, K. N. (2014). Toxicity, mechanism and health effects of some heavy metals. *Interdisciplinary Toxicology*, 7(2), 60–72. <https://doi.org/10.2478/intox-2014-0009>
- Jyothi, R. N (2020). Heavy Metal Sources and Their Effects on Human Health, Heavy Metals - Their Environmental Impacts and Mitigation, Mazen Khaled Nazal and Hongbo Zhao, IntechOpen, DOI: 10.5772/intechopen.95370. Available from: <https://www.intechopen.com/chapters/74650>
- Karakaş, F., Pyrgiotakis, G., Çelik, M.S. & Moudgil, B.M., (2011). Na-bentonite and MgO mixture as a thickening agent for water-based paints. *KONA Powder and Particle Journal* 29 (0): 96-106.

- Koncept Analytics, (2014)- Paint and coating market: future trends detailed. Retrieved Nov 11, 2021, https://issuu.com/prkonceptanalytics/docs/global_paints_and_coatings_sample_-
- Kazmierczak, J., Kempe, S., & Kremer, B. (2013). Calcium in the early evolution of living systems: a biohistorical approach. *Current Organic Chemistry*, 17(16), 1738-1750.
- Kumar, M. & Puri, A. (2012). A review of permissible limits of drinking water. *Indian Journal of Occupational and Environmental Medicine* 16 (1): 40–44.
- Manisalidis, I., Stavropoulou, E., Stavropoulos, A., & Bezirtzoglou, E. (2020). Environmental and Health Impacts of Air Pollution: A Review. *Frontiers in public health*, 8, 14. <https://doi.org/10.3389/fpubh.2020.00014>
- Nath, K., S. Shyam, D. Singh, & YK. Shanna. (2008). Effect of chromium and tannery effluent toxicity on metabolism and growth in cowpea (*Vigna sinensis* L. Saviex Hassk) seedling. *Research in Environment and Life Sciences*. 1: 91–94.
- Nazir, R., M. Khan, M. Masab, H.U. Rehman, N.U. Rauf, S. Shahab, N. Ameer, M. Sajed, M. Ullah, M. Rafeeq, & Z. Shaheen. (2015). Accumulation of heavy metals (Ni, Cu, Cd, Cr, Pb, Zn, Fe) in the soil, water and plants and analysis of physico-chemical parameters of soil and water collected from Tanda Dam kohat. *Journal of Pharmaceutical Sciences and Research* 7: 89-97.
- Ugonna C. Nkwunonwo, Precious O. Odika, Nneka I. Onyia, (2020). "A Review of the Health Implications of Heavy Metals in Food Chain in Nigeria", *The Scientific World Journal*, vol. 2020, Article ID 6594109, 11 pages, 2020. <https://doi.org/10.1155/2020/6594109>
- United Nations Environment Programme (UNEP). 2010. Final review of scientific information on lead. Retrieved Nov. 11, 2021, from http://www.unep.org/hazardoussubstances/Portals/9/Lead_Cadmium/docs/Interim_reviews/UNEP_GC26_INF_11_Add_1_Final_UNEP_Lead_review_and_appendix_Dec_2010.pdf
- Upadhaya, S. D., and Kim, I. H. (2020). Importance of micronutrients in bone health of monogastric animals and techniques to improve the bioavailability of micronutrient supplements - A review. *Asian-Australasian journal of animal sciences*, 33(12), 1885–1895. <https://doi.org/10.5713/ajas.19.0945>
- Sappino, A.P., R. Buser, L. Lesne, S. Gimelli, F. Béna, D. Belin, & S.J. Mandriota. (2012). Aluminium chloride promotes anchorage-independent growth in human mammary epithelial cells. *Journal of Applied Toxicology*. 32: 233-243.
- Talbert, R., (2007). *Paint Technology Handbook*. CRC Press. Grand Rapids, Michigan, USA. ISBN 1-57444-703-3.
- Tony Johnsen. (2006). Inert pigments, fillers, extenders. Retrieved Nov. 11, 2021, from http://www.paintmaking.com/inert_pigments.htm.
- Valko, M., Rhodes, C. J., Moncol, J., Izakovic, M. M. & Mazur, M. (2006). Free radicals, metals and antioxidants in oxidative stress-induced cancer. *Chemico-biological interactions* 160(1): 1-40.
- Vemula, M., V.B. R., Ambavaram, G. R., Kalluru, M. Gajulapalle, & N. K. V. Tollamadugu, (2013). "An Overview on Research Trends in Remediation of Chromium", *Research Journal of Recent Sciences* 2: 71-83.
- Williams, T.M., (2007). The mechanism of action of isothiazolone biocides. *Power Plant Chemistry* 9 (1): 14.
- World Health Organization (WHO) (2006). *Guidelines for drinking-water quality [electronic resource]: incorporating first addendum*. Vol.1, Recommendations. – 3rd ed.2006 .
- World Health Organization (WHO) (2010). - Joint Food and Agriculture Organization of the United Nations (FAO) Expert Committee on Food Additives. Seventy-third meeting. Geneva, 8–17 June 2010. SUMMARY AND CONCLUSIONS. Issued Jun. 24 2010. <http://www.who.int/foodsafety/publications/chem/summary73.pdf>
- Xu, J., Shi, H., Ruth, M., Yu, H., Lazar, L., Zou, B., ... & Zhao, J. (2013). Acute toxicity of intravenously administered titanium dioxide nanoparticles in mice. *PloS one*, 8(8): e70618.