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Assessment Of Some Heavy Metals in Some Plastic Toys Collected from Zawia City Markets

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تقييم بعض العناصر الثقيلة في بعض الألعاب البلاستيكية بمحلات مدينة الزاوية

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Abstract:
By fostering imagination, creativity, and the development of a variety of skills, toys are essential to a child's growth. Nevertheless, the presence of dangerous heavy metals like lead (Pb) and copper (Cu) in toy materials, especially plastic toys, can present serious health risks. This study sought to determine the concentrations of heavy metals (Cu, Pb, Cd) in plastic toys gathered from different Libyan markets in the city of Zawia. Ten distinct toy categories including jewelry, building blocks, balls, and animals were sampled. The concentrations of lead and copper in the samples were determined using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). According to the findings, the concentrations of lead varied from 0.37 mg/kg to 10.4 mg/kg, with an average of 2.14 mg/kg, and for copper varied from 0.56 mg/kg to 15.4 mg/kg, with an average of 4.613 mg/kg. The highest concentrations of lead and copper were found in colorful toys, even though the lead levels in all toy samples were below the 90 mg/kg maximum allowable limit. Due to their hand-to-mouth behavior and the metals' bioaccumulation, the study also emphasized the possible health risks of heavy metal exposure, particularly for younger children. It is advised that regulations be put in place to keep an eye on and manage the levels of heavy metal contamination in toys for kids. The results of this study help to increase public awareness about toy safety.

Keywords: Heavy metals, Plastic toys, ICP-OES .

الملخص
تلعب الألعاب دورًا مهمًا في تنمية الطفل، لكن احتواء بعضها، خاصة البلاستيكية، على معادن ثقيلة كالرصاص (Pb) والنحاس (Cu) يشكل خطرًا صحيًا. تهدف هذه الدراسة إلى قياس تركيزات (Cu, Pb, Cd) في ألعاب بلاستيكية من أسواق الزاوية، باستخدام مطيافية الانبعاث البصري المقترن بالبلازما الحث المزدوج. (ICP-OES) أظهرت النتائج أن تركيزات الرصاص تراوحت بين 0.37-10.4 ملغم/كغم (متوسط 2.14)، بينما النحاس 0.56-15.4 ملغم/كغم (متوسط 4.613). سجلت الألعاب الملونة أعلى التراكيز، رغم بقائها ضمن الحد المسموح به عالميًا (90 ملغم/كغم). ومع ذلك، فإن التعرض المزمن لهذه المعادن قد يؤدي إلى اضطرابات عصبية ومشاكل تنموية لدى الأطفال بسبب التراكم الحيوي والسلوكيات الفطرية كمصّ الالعاب وعضها. توصي الدراسة بفرض لوائح رقابية صارمة لمراقبة مستويات المعادن الثقيلة في الألعاب، وزيادة الوعي العام حول المخاطر الصحية المحتملة، إضافة إلى مزيد من الدراسات حول مصادر التلوث وتأثيره على صحة الأطفال.

الكلمات المفتاحية: العناصر الثقيلة، الألعاب البلاستيكية، بلازما الحث المزدوج المقترن بمطيافية الانبعاث الذري (ICP-OES) .

1. Introduction

A child's development depends heavily on toys, which are essential tools from birth and throughout life. Toys stimulate imagination, encourage creativity, and aid in the development of various abilities. However, it is crucial to understand the materials used in these toys to ensure children's safety and well-being. Children may unknowingly bite or handle toys improperly due to their ignorance and the potential toxicity of some of their components, which can be extremely dangerous. Plastic toys often contain harmful heavy metals in their outer paint coatings and core structure. Many of the synthetic materials used to make toys contain heavy metals such as lead (Pb), nickel (Ni), mercury (Hg), chromium (Cr), cadmium (Cd), silver (Ag), and gold (Au). The health of children is seriously endangered by these hazardous metals and the chemical compounds they contain, which can lead to a variety of ailments and diseases that negatively affect their well-being. Therefore, it is vital for parents and guardians to be aware of these dangers and choose safe, non-toxic toys to ensure the well-being of their children [1]. Children are especially prone to heavy metal exposure due to their hand-to-mouth behavior, lower body weight, and immature enzymatic systems. Exposure to toys containing heavy metals poses potential health risks, and the presence of certain heavy metals can lead to acute or chronic toxicity. The health effects associated with heavy metals in toys depend on the toxicity and duration of exposure, as well as the type of metal compound, its oxidation state, and bioavailability [2]. The potential health risks related to heavy metals in toys mainly come from oral ingestion and skin contact. Furthermore, these health risks have been widely considered in previous studies on toxic elements in toys. However, there has been no report on whether the carcinogenic risks involved in jewelry toys vary with wear locations or human activities. Carcinogens tend to accumulate in the deep epidermis, and absorption via the skin is typically a slow process. The absorption rate of toxic elements through the skin in adults is much slower than in the digestive system, suggesting that skin exposure to toxic elements is less of an external health risk [3]. Nonetheless, skin contact with toxic elements such as arsenic and lead, which are classified as heavy metal carcinogens (Group 1B) to humans according to the Globally Harmonized System of Classification and Labeling of Chemicals, is a concern. As such, it is recommended to assess the carcinogenic risks of heavy metals in toys via skin exposure, which has been largely overlooked. Previous research has shown that products containing heavy metals pose a higher carcinogenic risk [4]. Due to the possibility of bioaccumulation, exposure to heavy metals can pose long-term risks. Lead is one of the heavy metals that can cause learning disabilities, kidney failure, anemia, irreversible brain damage, and even death in children. Other metals, such as cadmium, can have various acute and long-term effects on the respiratory, gastrointestinal, and neurological systems. Cadmium, a known carcinogen, has been linked to lung, prostate, and kidney cancers [5]. Cheap plastic toys imported from international markets have become more widely available in Libya. However, no specific local laws exist to regulate or monitor the safety of these toys. Additionally, no studies have been conducted to determine whether these toys may expose children to heavy metal contamination. To ensure toy safety, it is crucial to assess the presence of these dangerous substances and implement preventative measures. The responsibility for safeguarding children's health is shared by governments, manufacturers, regulatory agencies, and parents. The current study aims to provide a comprehensive quantitative analysis of heavy metals (Cu, Pb and Cd) levels in plastic toys collected from various toy stores in Zawia. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is used to determine the levels and presence of these hazardous substances, evaluate potential health risks, and raise public awareness about the safety of children's toys sold in the local market.

2. Material and methods

2.1. Sampling

Ten plastic toys were purchased from different locations in Zawia markets. The toys were bright in color, available in largely darker shades of red, yellow, pink , blue, and green or a mix of these colors. Some were soft and easily squeezable while others were not flexible enough. the selected toys intended for two age groups, 1-3 years and 3-6 years. These included: Children’s jewelery, building blocks, cars, balls, plastic animals, fruit set, rubber ducks, ballons, whistles, and rattles

2.2. Sample Preparation and Treatment.

While the fragile samples were crushed into a powder, all plastic samples were chopped into pieces (about 0.5 cm). A sample weighing between 3.0 and 7 grams was placed in porcelain crucibles and burned on a hot plate until the fuming stopped. Complete ashing took place in a furnace set to 550–600°C for two hours. Following cooling, 10 milliliters of 70% nitric acid were added to the crucibles, which were then allowed to pre-digest for 24 hours at room temperature. After two hours of digestion at 130°C, the samples were cooled to room temperature. After that, this was filtered to the appropriate level with distilled water using Whatman No. 541 in a 50 ml volumetric flask. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was then used to analyze the samples for heavy metals. [6]

2.3. standards

A series of standard solutions for heavy metals, copper (Cu), and Lead (Pb), were prepared and measured, resulting in the calibration curves as shown in figure (1and2) with determination coefficients.

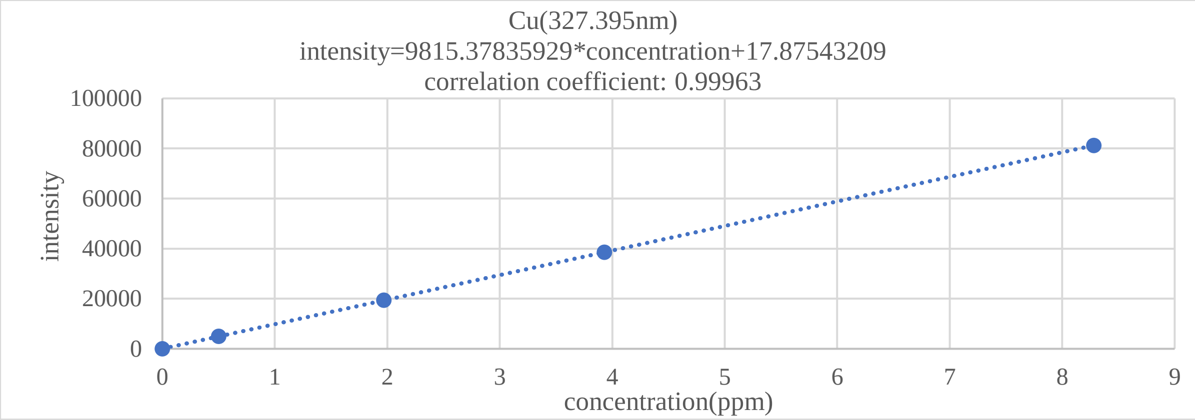

Figure (1): calibration curve for Cu.

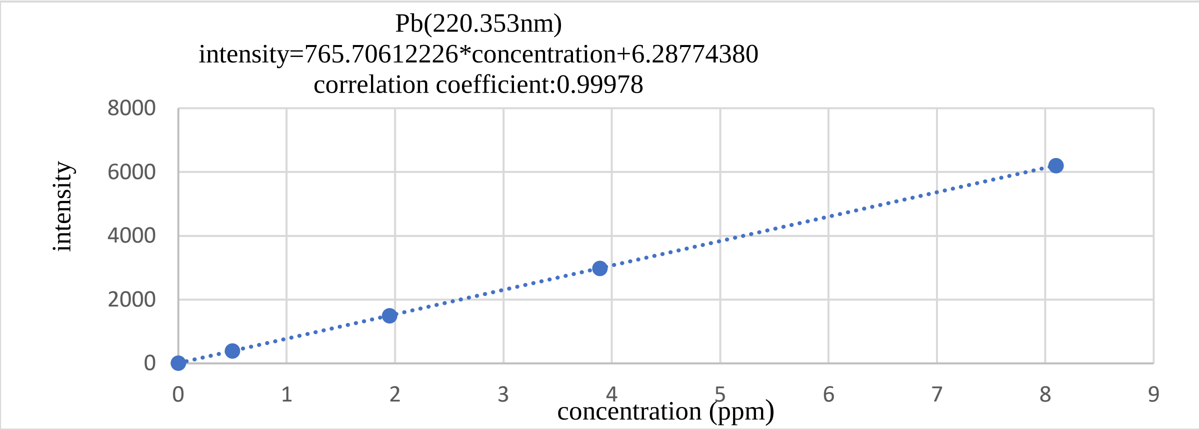

Figure (2): calibration curve for Pb.

2.4. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP - OES)

Analysis for heavy metal of interest was performed using inductively coupled plasma optical emission spectroscopy [Agilent 5110 ICP-OES] at the laboratory of Libyan petroleum institute. the limit of detection (L.D) of the analytical method for each metal was calculated as double the standard deviation of a series of measurements of a solution, the concentration of which is distinctly detectable above the background level. These values were 0.002, 0.003 mg/L for, Cu, and Pb, respectively. For the determination of these metals three solutions were prepared for each sample. The standard operating conditions for the analysis of heavy metals using (ICP-OES) used in our experiments are given in table (1,2) The means of these figure were used to calculate the concentrations

Table (1): ICP-OES instrument and method parameters.

Parameter	Setting
Viewing mode	Radial
Viewing height(mm)	8
Read time(s)	5
RF power(kw)	1.2
Stabilization time (s)	15
Nebulizer flow(l/min)	0.7
Pump speed (rpm)	12
Plasma flow(l/min)	12
Sample introduction	Manual
Sample uptake time (s)	25
Replicates	3

Table (2): wavelength, working, and calibration range.

Element	Wavelength(nm)	Background correction	Calibration fit
Cu	327.395	Fitted	Liner weighted
Pb	220.353	Fitted	Liner weighted
Cd	214.439	Fitted	Liner weighted

3. Results and discussion

The average concentration, stander deviation and R.S. D% of copper (Cu) and lead (Pb) in the toy samples collected from Zawia City markets are presented in Table (3), (4). column diagram of the same data is presented in figure 3 and 4 respectively.

3.1 Copper (Cu)

The results obtained concluded that the concentration of copper ranged between (0.56 to 15.4) mg/kg, while the average was 4.613 mg/kg, this result agreement with the study conducted by Sharifah N., Nurul S. (2017). the highest concentration was in blue whistle sample1 which is less than the maximum allowable value according to international stander 622.5mg/kg [7], while the lowest concentration was in red car Sample.

Table (3): Concentration of copper Cu in samples (ppm).

Samples	Concentration (mg\kg)	Mean of con. (mg\l)	S.D	R.S.D%
Blue whistle	15.4	2.315	0.245	10.5
Orange rattle	3.1	0.310	0.06	19.35
Green building block	4.3	0.43	0.094	22.0
Pink jewelry	5.7	0.40	0.01	2.5
Yellow duck	1.37	0.085	0.005	5.88
Red car	0.56	0.056	0.009	16.87
Yellow ball	4.25	0.315	0.015	4.7
Colorful animal set	3.25	0.325	0.005	1.5
Colorful fruit sets	4.05	0.405	0.119	29.5
Colorful balloons	4.15	0.415	0.035	8.4

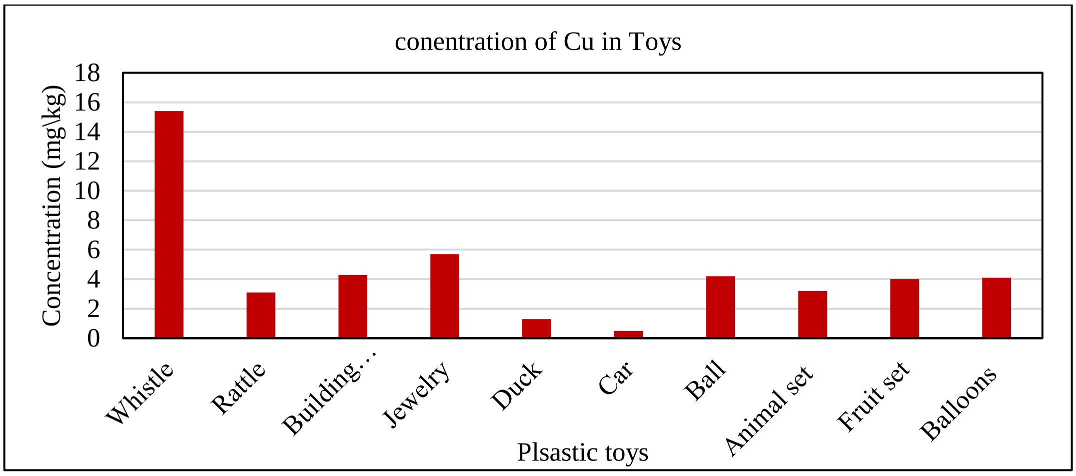

Figure (3): concentration of Cu in toys.

3.2 Lead (Pb)

The results showed that the concentration of lead ranged from 0.37to10.4 with an average 2.14mg/kg this result agrees with the study conducted by G Y Al Kindi, Z H Ali (2020) [8] . All the toy samples were found to contain lead with concentration lower than 90mg/kg, which is less than the maximum allowable value according to international stander [9]. The highest concentration of lead was in animal set Samples, while the lowest concentration was in the pink jewelry Samples.

Table (4): Concentration of lead Pb in samples (ppm).

Samples	Concentration (mg\kg)	Mean of con. (mg\l)	S.D	R.S.D%
Blue whistle	1.97	0.296	0.0365	12.36
Orange rattle	1.2	0.12	0.0081	6.8
Green building block	1.23	0.123	0.0124	10.1
Pink jewelry	0.37	0.026	0.0042	16.2
Yellow duck	1.12	0.07	0.01	14.2
Red car	0.85	0.085	0.015	17.64
Yellow ball	0.81	0.06	0.00	0.0
Colorful animal set	10.4	1.04	0.099	9.5
Colorful fruits set	1.05	0.105	0.005	4.76
Colorful balloons	2.4	0.24	0.01	4.16

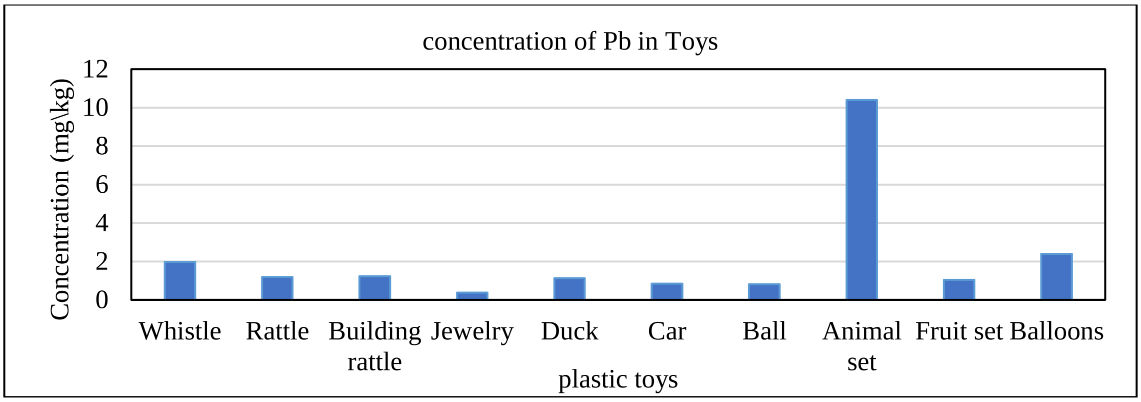

Figure (4): concentration of Pb in toys.

3.3 Cadmium (Cd)

According to the extraction and analysis method used here, the results of this study showed that cadmium was below the detection limit in all the samples studied, which is in agreement with the study conducted by Ishmail K (2023) [10] which showed that cadmium concentration was BDL.

The absence of concentration of this metal in the samples of this study may be due to that metal does not enter into the composition of the surface of plastic materials of the studied toys or not used as printing material in the sample toys or a coloring pigment in the paint of the toys.

Table (5): Concentration of cadmium Cd in samples (ppm).

Samples	Mean of con. (mg\l)
Blue whistle	0.000
Orange rattle	0.000
Green building block	0.000
Pink jewelry	0.000
Yellow duck	0.000
Red car	0.000
Yellow ball	0.000
Colorful animal set	0.013
Colorful fruits set	0.000
Colorful balloons	0.003

By comparing the concentrations of both copper and lead in samples of children's toys according to their ages, as in Figures 4 and 5, we found that the highest concentration of copper (15.4ppm) was in the toys of children between the ages of 3 and 6 years, while lead was in the sample of toys of children between the ages of 1 and 3 years .However, even though the lead concentration is less than the permissible limit, it is considered dangerous for children at this age because no matter how small the pollutants are, they appear in children at puberty [11].

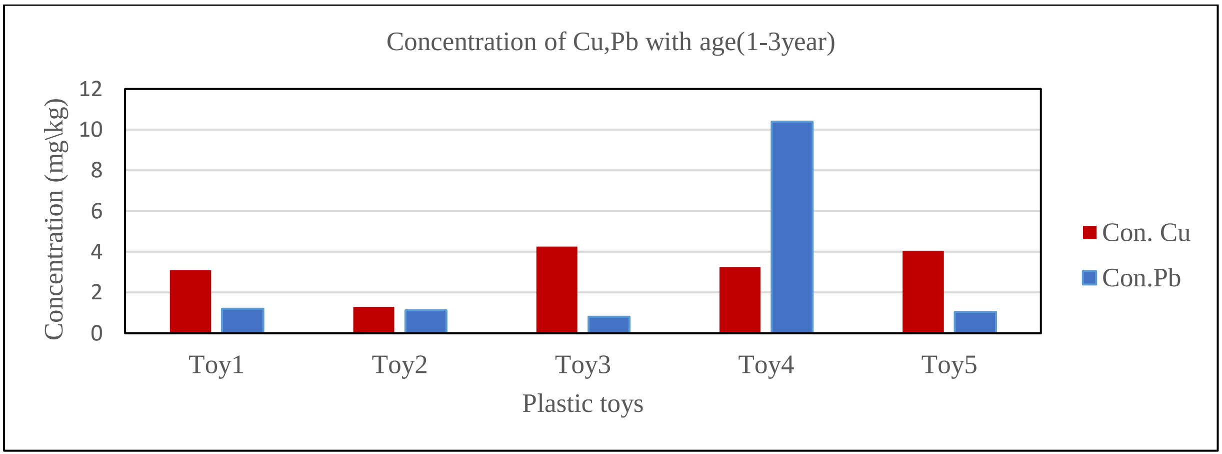

Figure (5): concentration of heavy metal with age (1-3 year).

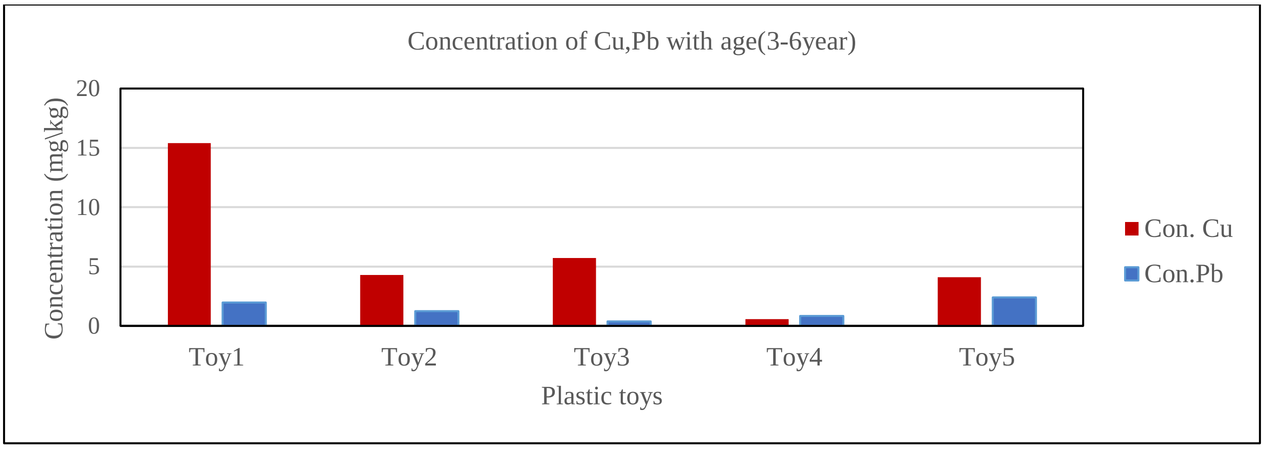

Figure (6): concentration of heavy metal with age (3-6 year).

From the graph in figure (7,8) , it is clear that there is a clear difference between colorful toys and toys with one color, where we find that the highest concentration of lead appears in the sample of colorful animals set(10.4mg/kg), while there is no clear difference between the concentration of green(1.23 mg/kg), yellow (1.12 mg/kg)and orange(1.2 mg/kg) samples , as for copper element , according to the graph in figure (6), it appears that its highest concentration was also in blue sample , where the copper concentration reached 15.4 mg/kg. Therefore, it can be said that the higher the percentage of color in the sample, the higher the concentration of heavy metals in it, and the darker color , the higher percentage of these elements ,where the blue sample showed the highest concentration of copper and lead after the colorful samples , as their concentration were 15.4 mg/kg and 1.97 mg/kg respectively .This is consistent with study of G Y Al Kindi and Z H Ali , which was conducted in 2020 and study of Reem A. Alsaigh , Hayat S. Althobaiti , in 2024 [12] .

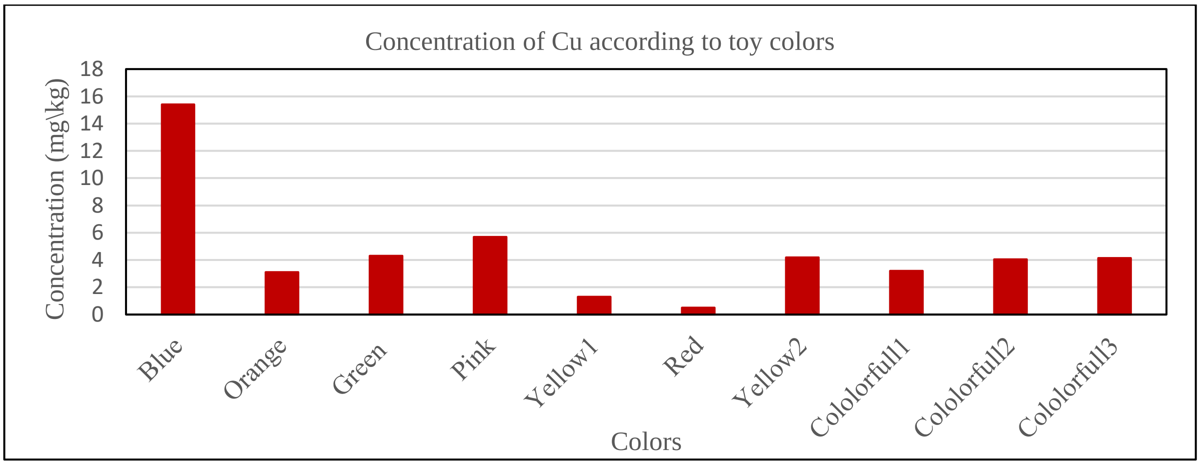

Figure (7): concentration of Cu according to toy colors.

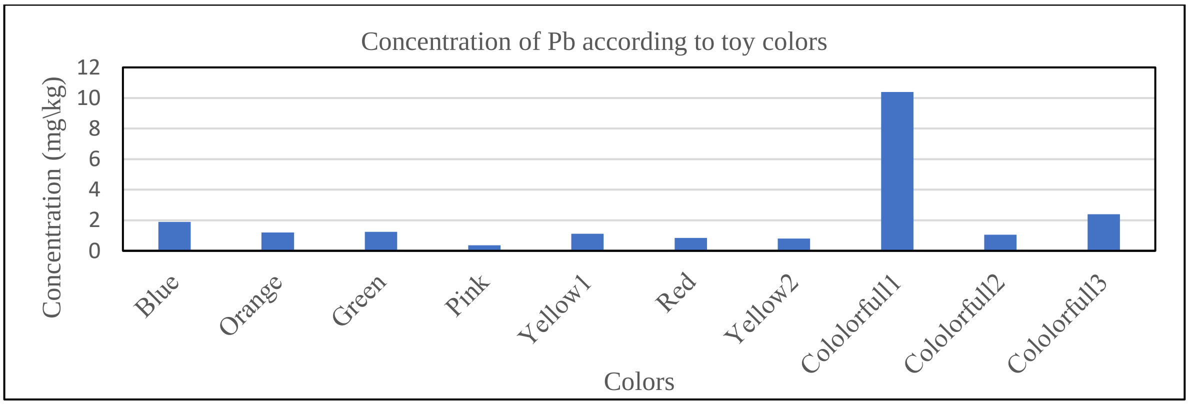

Figure (8): concentration of Pb according to toy color.

4.Conclusion

This study showed that the concentration of copper was higher than the concentration of lead in the studied plastic toys samples, and it also showed the absence of cadmium in them. The highest concentration of copper appeared in the toys of children between the ages of 3 and 6 years, while the highest concentration of lead was in the toys of children between the ages of 1 and 3 years. As for the relationship between color and the concentration of copper and lead, the concentration was higher in the dark-colored samples, followed by the samples with mixed colors. Although these concentrations are less than the permissible limits, However, the presence of these elements, even in small concentrations, is considered dangerous because they accumulate in the bodies of children who play with these toys. Therefore, we recommend tightening control over these products.

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