Libyan Journal of Ecological & Environmental Sciences and Technology
(LJEEST)

LJEEST
ISSN: 2710-5237
www.srcest.org.ly/jou

DOI: https://doi.org/10.63359/4kyqd694

Evaluating the Levels of Soluble Fraction in Artificial Saliva and Gastric Solution of Several Toxic Metals from Coloured Plastic Toys Linking to the Associated Health Risk Index

Salem Irhema Irhema*, Nour ALhuday Abdalla Jumha, Heba Abdulqadir Abraheem

ARTICLE INFO

Vol. 7 No1 April 2025.
Pages (64 - 72)

Article history:
Revised form 27 February 2025
Accepted 30 March 2025

Authors affiliation
Environmental Sciences Department, Faculty of Science, University of Al-Zintan, Libya.
Corresponding author

Email: s.irhema@uoz.edu.ly
0000-0001-5428-1993

Keywords:
Gastric Solution, Health Risk Index, Plastic Toys, Saliva, Toxic Metal.

ABSTRACT

Several toxic metals are presented in children's coloured plastic toys due to the addition of some of their compounds as stabilisers, painted agents and chemical and weather resistant layers. Unfortunately, fractions of hazardous metals may become bio-accessible to children's saliva and gastric juices as result of hand-mouth behaviour ending up in the stomach. Thus, fourteen samples of most purchased coloured plastic toys were collected from markets in the western-mountain area in Libya. The aim was to evaluate the soluble fractions of Al, Cd, Cr, Mn, Ni, Pb, Sb, Sn and Zn in artificial saliva and 0.07 M HCl (simulating gastric solution) and based on the bio-accessible fractions of studied metals, calculate the associated health risk index (HI). The results demonstrated that the soluble fraction of Mn, Pb, Sb, Sn and Zn in saliva extractions was lower than the permissible levels of these metals set by EU countries. Findings indicated however that the levels of soluble fractions of Al in 100% of toys, Cd in 50% of samples, and Cr in 21% of samples migrated from the target toys to children saliva exceeding the allowable levels of these metals set by EU countries. Additionally, the concentrations of target metals in simulated gastric solution exceeded the limits of these metals set by EU countries for Cd in 57% of samples, Cr in 43% of toys and Pb in 50% of studied samples, but the levels of Al, Mn, Ni, Sb, Sn, and Zn in acid solution were below the limitations of these metals in the same solution recommended by EU countries. The HI values showed variation among metals and solutions reporting high risk in the case of Al in saliva, Mn and Ni in both solutions, Cd in most samples of both extractions and Pb in most samples of acid extraction. In conclusion, the use of these toys may cause harmful health effects to children that play with them for prolonged periods evidenced by the presence of a target metal in most acid and saliva extractions.

تقدير تركيز الجزء الذائب في محلولين اصطناعيين للعاب وحمض المعدة لبعض العناصر الكيميائية السامة المتواجدة في العاب الأطفال البلاستيكية الملونة وربطه بمؤشر الخطر الصحى المتوقع

سالم رحيمة سالم رحيمه*، نورالهدى عبدالله جمعه الصغير، هبة عبدالقادر إبراهيم

تدخل بعض العناصر الكيميائية السامة في صناعة العاب الأطفال البلاستيكية كمثبطات ومواد ملونه ومواد تجعل من هذه الألعاب تقاوم الكيماويات وتأثيرات البيئة المحيطة. ولكن وجدت دراسات عديده ان كميات مختلفة من هذه العناصر تذوب في لعاب ومحلول معدة الأطفال الذين يلعقون ويبتلعون جزاً من هذه الألعاب. لذلك ولان هذا النوع من الألعاب كثير التداول بين الأطفال في ليبيا فتم تجميع 14 عينه من أكثر الألعاب مبيعا ببلديتي الأصابعة والزنتان بالجبل الغربي، بهدف تقدير تركيز الطور الذائب من Al, Cd, Cr, Mn, Ni, Pb, Sb,Sn, Zn في محلولين اصطناعيين للعاب الأطفال وحمض المعدة ومن ثم حساب مؤشر الخطر الصحى (HI) الناتج من ذوبان هذه العناصر في المحاليل الحيوية لأجسام الأطفال. وقد بينت النتائج أن تركيز العناصر Mn, Pb, Sb, Sn, Zn في مستخلص اللعاب الاصطناعى كان اقل من تلك المسموح بها من قبل دول الاتحاد الأوربي في نفس النوع من المستخلص. ولكن كان تركيز الجز الذائب في محلول اللعاب من كلا من Al في 100% من العينات وCr في 21% من العينات وCd في 50% من الألعاب قيد البحث اعلى من حدود هذه العناصر المسوح بها من قبل الاتحاد الأوربي. اما بالنسبة لتراكيز العناصر المدروسة في محلول حمض المعدة فكان Cd في 75% من مستخلص العينات وCr في مستخلص 43% من العاب الأطفال وPb في 50% من مستخلص الألعاب المستهدفة اعلى من الحدود المسموح بها من قبل الاتحاد الأوربي لهذه العناصر في مستخلص المعدة الحامضي، بينما كانت تراكيز Al وMn في محلول المعدة اقل من تلك المسموح بها من قبل الاتحاد الأوربي. أما قيم مؤشر الخطر الصحى (HI) فقد أظهرت تباين فيما بين العناصر والمستخلصين، فكانت القيم عالية في حالة الالومنيوم في مستخلصات اللعاب والمنجنيز والنيكل في كلا المستخلصين، والكادميوم في معظم عينات محلولي الاستخلاص والرصاص في معظم عينات المستخلص الحامضى. وبناء على ذلك فان استخدام هذه الألعاب من قبل الأطفال يجعلهم عرضة لتراكم هذه العناصر السامه في اجسامهم مسبباً اخطار صحية لهم مع الزمن.

INTRODUCTION

Children coloured plastic toys may contain hight concentrations of several toxic metals such as Aluminium (Al), Antimony (Sb), Arsenic (As), Cadmium (Cd), Cobalt (Co), Copper (Cu), Lead (Pb), Manganese (Mn), Mercury (Hg), Nickel (Ni), and Zinc (Zn) (Shahzad et al., 2022a). The presence of these metals in plastic toys is due to use of some chemicals as stabilisers in plastic manufacturing e.g., $CdCO_3$ and CdO (Echa, 2012), dicarboxylates of Cd, Pb and Zn or/and adding several heavy metal compounds to paints with different colours to minimise the weather and light effect, thermal stability and chemical resistance during the process of making coloured toys (Turner and Filella, 2021). These additives including lead chromate ($PbCrO_4$) gives toys colours ranging from yellow to orange, red lead oxide (Pb_3O_4) in red paint, a mixture of Ni and Cu in yellowish pink paint, basic lead carbonate $PbCO_3$-$Pb(OH)_2$ for a white colour dye. Also, MnO a green crystalline powder (Wright, 2003; Irhema, 2006), Cadmium sulphide (CdS) a yellow pigment, Cobalt (II) diacetate (Co $(CH_3COO)_2.4H_2O$) a blue paint (Turner and Filella, 2021) and Chromic chloride ($CrCl_3$) in preparing green pigment (Cui et al., 2015). In addition, Zinc oxide (ZnO), Antimony oxide (Sb_2O_3) and Arsenic 10-10´-oxybisphenoxarsine are applied to plastic toys as a fungicide and antimicrobial agents (Janssenet al., 2016). All these pigments providing colour also increase the toys' brightness to attract the attention of children when shopping (Shahzad et al., 2022b). In addition to these heavy metals, Al is widely used in the manufacture of plastic (BURG, 2015). Globally, many studies have reported the presence of hazardous metals by various levels in toys and jewellery and their migration to children's saliva and gastric solution. The hand-mouth behaviour of young children during play with the coloured plastic toys, specifically at age of 6 – 12 months, was estimated by 39 – 66 minute daily. This leads to mobilisation of a toy's toxic metals to the child's saliva and they may ingest some plastic particles into gastric system. Due to the effect of acid solution in the stomach, the toxic metals from the plastic become available to translocate within human body through blood stream causing damage and severe health issues (Cui et al., 2015). In this contexts, Kamara et al. (2023) stated that children coloured plastic toys sold in Nigeria contain various levels of Cd, Mn, Ni, and Pb, and different fractions of these metals can be extracted from these toys by children's saliva and gastric solution facilitating their movement to human organs. Fadaei (2023) reported that, several developing and developed countries have issued legalisations to control the application of toxic chemicals including heavy metals to plastic toys and jewellery during the manufacturing process. Unfortunately, these items sold in numerous countries still contain various levels of Al, As, Cd, Co, Cr, Cu, Hg, Ni, Pb, and Sb. The presence of these metals in human body can cause severe health problems, even though some of these metals are essential to human body at low intake levels e.g., Cu, Co and Zn. However, high intake of concentrations of these metals and any levels of non-essential metals such as Pb and Cd are extremely poisonous. The toxicity route of these metals is similar including: damaging the haematopoietic system, oxidative stress of antioxidant defence and inhibiting the activity of enzymes involved in plant and animal cell division (Shahzad et al., 2022a). Weidenhamer and Clement (2007a) reported that a child has died due to Pb poisoning in 2006 in the USA because of swallowing a jewellery charm. Kamara et al. (2023) stated that many investigations have been conducted to determine the pseudo-total levels of hazardous metals in coloured plastic toys, however limited studies have explored the bio-accessibility of toxic metals in children's body secretions due to mouthing and swallowing coloured plastic toys. In this context, some chemical solutions simulating the real children saliva and gastric contents were used to evaluate the fraction of toxic metals that may migrate to these solutions from toys. It is recommended that further studies to discover the portions of hazardous metals that may become soluble in the saliva and gastric medium of children during play. Because of the Libyan markets are open to most countries, particularly China and Egypt for the importation of cheap children's coloured plastic toys without specific monitoring and legalisation to control the trade on toys. And to our knowledge, no studies were discovered investigating the bio-accessible concentrations of toxic metals that might be extracted by children's saliva and gastric solution from plastic toys sold in Libya and associated health risks in order to protect our childrens' health. Accordingly, this work aimed at; 1) estimating the fraction of Al, Cd, Cr, Mn, Ni, Pb, Sb, Sn, and Zn migrating to artificial children saliva as a result of mouthing imported toys in particular Chinese and Egyptian coloured plastic toys ; 2) evaluating the fraction of target metals that become bioavailable due to the effect of the acid medium of children's stomachs due to the ingesting of pieces of Chinese and Egyptian coloured plastic; and 3) calculating the health risk index based on the bio-accessibility fractions of studied metals.

MATERIALS AND METHODS

Sample collection

Fourteen toys frequently bought by local families were purchased from two markets in Alassaba and Al-Zintan municipalities. Some of toys sample is shown in figure (1). The collected samples were transported to the laboratory and washed by tap water and then by double-distilled water and dried in air for a week before the parts with the same colour of any toy were selected. The chosen dried part of sample was cut into small pieces and kept in paper bags until analysis of target soluble fractions in artificial saliva and gastric solutions using bio-accessibility tests.

Estimating the Fraction of Target Metals Migrating to Artificial Children Saliva

According to the method reported by Kamara et al. (2023), 2.23g of a sample in triplicate (see the limitation section) was weighed accurately and put in conical flask with stopper then adding 25 ml of fresh artificial saliva solution to the sample. The artificial saliva was prepared by dissolving 4.5g of NaCl, 0.3g of KCl, 0.3g of Na_2SO_4, 0.4g NH_4Cl, 3g lactic acid and 0.2g urea in 1L of double-distilled water. The stoppered conical flask was put in the Erlenmeyer shake for 5 hours at room temperature (25°C) before the extract was quantitively filtered through Whatman filter paper No:42 in Pyrex classed tubs, the residues of plastic pieces being kept for the next step in the process. The labelled tubs were sent for analysis of the fraction of target metal that migrated to the saliva from the surface of plastic toys by XRF Spectrometer Cube.

Evaluating The soluble Fraction of Target Metals Migrating to Children's Gastric Solution

25 ml of 0.07N HCl solution with a pH ranging from 1.8 to 2.2 simulating the stomach environment (prepared from 35.4% HCl BDH Analar grade free of heavy metals) was added to the washed residues of the previous step in a clean stoppered conical flask. The flask was put in the Erlenmeyer shake for 5 hours at room temperature 25°C before being quantitively filtered through Whatman filter paper No:41 in Pyrex classed tubs (Kamara et al., 2023). The labelled tubs were sent for analysis to discover the concentration of target metals solubilised in the gastric solution from the plastic toys using XRF Spectrometer Cube. For both steps, two blank solutions were prepared separately by following the same procedure without toy pieces and measured to use in the calculation of results.

Figure (1). Some of investigated plastic toys

Statistical Analysis:

The concentration of target metals was calculated by subtracting the metals concentration in the blank sample from the levels of metals in the measured sample and the results currently in mg/l converted to values in mg/kg and all calculations run by using a version 2501 of Excel software.

Health Risk Assessment

According to Cui et al. (2015), the health risk assessment can be estimated by calculating the hazard index (HI) as a result of plotting the chemical daily intake (CDI) for both saliva and ingestion situations based on the levels of target metals in artificial saliva and gastric solution. The children aged 6–12 months were chosen because of their common hand-mouth behaviour of licking, mouthing, biting and chewing plastic toys. The CDI for both saliva and ingestion situations and HI are calculated following Equations (1- 3).

$$\mathbf{CDIsaliva = Qbio\ \ ED / BW} \qquad \mathbf{(1)}$$

Where CDIsaliva is the CDI mouthing ($mg\ kg^{-1}\ d^{-1}$), Qbio is the concentration of target metal extracted by saliva based on 10g of toys sample during the time of shaking (5h), ED is the time of mouthing the toy by children as it estimated to be 66 min d-1 for age 6–12 months and BW is the average body weight of children of this age = 9.2 kg.

$$\mathbf{CDI\ ingestion = Qbio\ \ EF / BW} \qquad \mathbf{(2)}$$

Where CDIingestion is the CDI ingestion ($mg\ kg^{-1}\ d^{-1}$), Qbio is the concentration of target metal extracted by gastric acid solution based on 10g of ingested toys sample, EF is the exposure regularity (1 day expected exposure) and BW is the average body weight of children at age of 6–12 months = 9.2 kg.

$$\mathbf{HI = CDI / RfD} \quad \mathbf{(3)}$$

RESULTS AND DISCUSSION

The obtained and calculated findings of soluble fractions of target metals and associated HI values are presented in tables 1, 2 and 3 and discussed as follows:

Metals fraction migrating to artificial saliva

The concentration of studied metals extracted by artificial saliva from target plastic toys is presented in table (1) below.

Al:-

The migrating levels of Al from the studied samples to artificial saliva recorded high levels more than the permissible levels set by EU countries (1406 mg Kg $^{-1}$) ranging from 1926 mg kg^{-1} in a yellow car toy manufactured in Egypt to 3557 mg kg^{-1} in a blue penguin made in Chain. These results confirm that, the solubility of Al is high in the children's saliva posing extreme risks to the playing children by prolonged use of these toys particularly as Al can cause several cancers, Alzheimer diseases and some skin infections (Klotz et al., 2017).

Cr: -

The concentrations of Cr artificial saliva extraction were unmeasurable in 57% of toy samples however, the levels of soluble Cr in multi-colour balloons imported from China recoded 10.1 mg kg^{-1}, 5.27 mg kg^{-1} in a red car produced in China and 6.28 mg kg^{-1} in white kitchen equipment sourced from Egypt. These values were exceeding the EU countries standard (4.8 mg kg^{-1}) for Cr migrated from plastic toys to children's saliva. The presence of Cr in the human body may affect the respiratory and immune systems, damage the liver and kidneys and the exposure to high levels of Cr for long term may cause lung cancer (Mračević et al., 2022).

The results obtained for Cr are higher than recorded levels ranged from below the machine limit of detection to 0.93 mg kg^{-1} found by Cui et al. (2015), and (Karas and Frankowski, 2018) (0.058 – 0.888 mg kg^{-1}), also higher than that found by Kamara et al. (2023) recording unmeasurable levels of Cr in saliva extraction from plastic toys. However, the current study findings are lower than that found by Al-Qutob et al. (2014) (10.50 0.45 – 33.7 0.74 mg kg^{-1}).

Mn:-

The concentrations of Mn in all toys studied showed lower values more than 10-fold less than the allowable levels set by EU countries (300 mg kg^{-1}), ranging from 6.39 mg kg^{-1} for a yellow car made in Egypt to 29.04 mg kg^{-1} in a white Bear imported from China, which suggests that these toys are safe for Mn toxicity levels. These results are higher by more 100-fold than those found by Kamara et al. (2023) for Mn (< 0.001 – 0.053 mg kg^{-1}).

Table (1). The concentration of studied metals in target plastic toys extracted by artificial saliva (mg kg^{-1}).

Sample Code	Sample type	Sample colour	Producer	Al	Cr	Mn	Ni	Zn	Cd	Sb	Pb	Sn
			Studied metals									
1	Car	Yellow	China	**2299**	1.68	25.67	1.46	1.12	**2.80**	13.45	0.90	BD
2	Balloons	Multi colours	China	**1999**	**10.1**	27.91	2.02	0.67	**3.92**	7.85	1.12	BD
3	Frog	Green	China	**5612**	BD	11.10	3.25	1.01	BD	BD	1.68	7.85
4	Kitchen items	Orange	China	**1982**	BD	13.34	**17.83**	1.68	**1.12**	2.24	0.78	5.61
5	Pokemon	Yellow	China	**2006**	BD	10.54	4.37	2.24	0.22	1.12	0.67	5.61
6	Penguin	Blue	China	**3557**	1.35	20.18	1.79	4.04	**3.81**	12.33	BD	BD
7	Bear	White	China	**2258**	1.35	29.04	3.14	0.56	**4.48**	11.21	1.12	BD
8	Car	Red	China	**2290**	**5.27**	33.52	2.02	2.02	**3.03**	13.45	BD	BD
9	Car	Blue	China	**5811**	BD	11.10	11.32	1.23	BD	BD	1.46	7.85
10	Gone	Dark red	China	**2103**	BD	13.34	10.20	1.68	BD	1.12	1.68	10.09
11	Kitchen items	white	Egypt	**2723**	**6.28**	18.95	1.91	2.02	**3.48**	10.09	0.22	BD
12	Car	Yellow	Egypt	**1926**	BD	6.39	0.24	1.46	BD	0.56	0.67	6.73
13	Car	Blue	Egypt	**1950**	BD	7.74	10.09	0.34	BD	0.90	1.01	8.97
14	Car	Pink	Egypt	**2232**	BD	6.61	8.52	1.01	BD	2.24	BD	3.36
EU standards			European Union	1406	4.8	300	18.8	983	0.3	60	2	12*

*(Turner & Filella, 2021)

Ni: -

The levels of Ni in all examined samples were lower than the value suggested by EU countries (18.8 mg kg^{-1}) for Ni that may have migrated to saliva from plastic toys and ranged in all samples from 0.24 mg kg^{-1} in Egyptian toy car coated with yellow paint to 17.83 mg kg^{-1} in orange kitchen items sourced from China. These results are higher than that found by Cui et al. (2015) in jewellery and toys sold in several markets in Nanjing- China (not detected levels – 0.26 mg kg^{-1}) and higher than that observed by Mračević et al. (2022).

Zn:-

The migrated levels of Zn to artificial saliva ranged from 0.34 mg kg^{-1} in a blue car imported from Egypt to 4.04 mg kg^{-1} in a blue penguin made in China, revealing the studied samples contain levels of Zn much lower than the allowable soluble concentration migrated to saliva from toys set by EU countries (983 mg kg^{-1}). The findings of this study are much lower than that found by Al-Qutob et al. (2014) investigating metal migration to artificial saliva from coloured plastic toys solid in Palestine (15 0.94 to 112 3.02 mg kg^{-1}).

Cd:-

Cadmium was undetectable in several analysed samples (3, 9, 10,12, 13 and 14), though in the rest of the studied samples the Cd concentrations migration to saliva solution ranged from 0.22 mg kg^{-1}, as in a yellow Pokemon made in China, to 4.48 mg kg-1 analysed from a white Bear imported from China. Cd levels in artificial saliva obtained in this study are higher than that recommended by EU countries (0.3 mg kg^{-1}) in 50% of target toys extractions (Karcioglu et al., 2022). Cd has the ability to accumulate biologically in the human body's soft tissue e.g.,liver, kidney and bone marrow posing several health effects to these organs. The results of this study for Cd are closed to that obtained by Cui et al. (2015) (not detectable – 0.93 mg kg^{-1}).

Sb:-

Antimony showed levels in saliva extractions of studied samples ranging from 0.65 mg kg^{-1}in a yellow car made in Egypt to 13.45 mg kg-1 in a yellow car exported from China to Libya. In samples 3 and 9 the Sb recorded concentrations below the machine limit of detection. Thus, the Sb levels obtained in this investigation were lower than that set by EU countries (60 mg kg^{-1}). The findings of this study are higher than that reported by Cui et al. (2015) for Sb in saliva extraction transferred from plastic toys (not detectable – 0.19 mg kg^{-1}), but lower than that found by Karas and Frankowski (2018) for Sb migrated to children saliva from painted plastic toys (339 – 3066 mg kg^{-1}).

Pb:-

Lead was undetectable in 21.4% of the investigated sample saliva solution, conversely Pb levels ranged from 0.22 mg kg^{-1} in white kitchen equipment extractions sourced from Egypt to 1.68 mg kg-1 in a green frog and dark red gnome saliva solutions both produced in China. As a result, the Pb levels in artificial saliva extractions of assessed toys were lower than it's acceptable concentrations set by EU countries. These results of Pb in saliva are in the range of that stated by Kamara et al. (2023) (not detected – 42.4 mg kg^{-1}), but less than that found by Karas and Frankowski (2018) ranging from 3.33 to 7.10 mg kg^{-1} also lower than the result obtained by Al-Qutob et al. (2014) in the same extractions (9.40 1.37 – 45.20 1.02 mg kg^{-1}).

Sn:-

Tin was unmeasurable in 43% of investigated sample saliva solutions but ranged from 3.36 mg kg^{-1} in a pink car imported from Egypt to 10.09 mg kg^{-1} in a dark red gnome produced in China.

Metals fraction migrated to children's gastric solution:

The obtained results of studied metals (mg kg^{-1}) extracted by simulated gastric solution (0.07 M HCl) from target plastic toys are illustrated in table (2).

Al:-

The Aluminium levels extracted by artificial stomach solution were much lower than that recommended by EU (1406 mg Kg^{-1}) and ranged from the lowest detection limit in white kitchen equipment, sourced from Egypt to 207 mg kg^{-1} in multi-colour balloons acid solution imported from China.

Table (2). The levels of studied metals (mg kg^{-1}) in target plastic toys extracted by simulated gastric solution (0.07 M HCl).

Sample Code	Sample type	Sample colour	Studied metals level									
			Producer	Al	Cr	Mn	Ni	Zn	Cd	Sb	Pb	Sn
1	Car	Yellow	China	6.73	**11.21**	31.39	1.12	BD	**4.48**	15.70	**3.59**	0.56
2	Balloons	Multi colours	China	207	2.91	14.57	**29.15**	54.93	**1.12**	6.73	BD	12.89
3	Frog	Green	China	6.73	**8.63**	25.78	BD	1.12	**4.48**	BD	**2.47**	0.45
4	Kitchen items	Orange	China	6.73	**9.42**	28.03	1.12	1.91	**4.48**	15.70	0.22	0.34
5	Pokemon	Yellow	China	6.73	BD	2.24	6.28	1.12	BD	3.36	1.35	9.53
6	Penguin	Blue	China	4.48	BD	1.79	3.59	1.12	BD	3.36	**2.47**	10.65
7	Bear	White	China	4.48	BD	1.23	4.04	1.12	BD	3.36	0.78	9.53
8	Car	Red	China	6.73	**5.04**	23.54	1.12	2.24	**4.48**	16.82	**2.47**	17.38
9	Car	Blue	China	6.73	**6.50**	24.66	1.12	3.36	**4.48**	BD	0.78	0.56
10	Gone	Dark red	China	4.48	BD	1.57	6.84	1.12	BD	3.36	**2.47**	6.17
11	Kitchen items	white	Egypt	BD	BD	2.58	2.02	1.12	BD	3.36	1.35	7.29
12	Car	Yellow	Egypt	7.85	**7.74**	29.15	1.12	0.78	**4.48**	15.70	0.22	0.22
13	Car	Blue	Egypt	207	BD	8.97	6.95	0.78	**1.12**	5.61	**2.47**	10.65
14	Car	Pink	Egypt	4.48	BD	1.23	4.48	1.12	BD	3.36	**2.47**	9.53
EU standards			European Union	1406	4.8	300	18.8	983	0.3	60	2	12*

*(Turner & Filella, 2021)

Cr:-

Chromium levels were higher than that suggested by EU countries (4.3 mg kg^{-1}) in 43% of acid extractions of studied samples and ranged from undetectable levels in 50% of target samples to 11.21 mg kg^{-1} in the Chinese fabricated yellowish car acid solutions. Kamara et al. (2023) reported that extracted Cr from toys by gastric solution was undetectable. The findings of this study are less than that observed for the concentration of Cr in acid medium simulating that of human stomach solution (11.5 0.74 – 33.7 0.74 mg kg^{-1}), and in line with that obtained by Astolfi et al. (2020) (unmeasurable – 4.0 mg kg^{-1}).

Mn:-

The concentrations of Mn in all target toys acid extractions were lower by more than 10-fold than the amount set by EU countries (300 mg kg^{-1}) and ranged from 1.23 mg kg^{-1} in the extractions of samples 7 and 14 to 31.39 mg kg^{-1} in a yellow car toy made in China acid solution. The observed data are in the range of the levels of Mn that has migrated to artificial gastric solution from toys described by Astolfi et al. (2020) (0.22 – 164 mg kg-

^{1}) and higher than that stated by Kamara et al. (2023) (not detected – 1.24 mg kg^{-1}).

Ni:-

The Ni level in gastric juice samples obtained in multi-coloured balloons manufactured in China was higher than the acceptable level of Ni set by EU (18.8 mgkg^{-1}) and ranged from below machine detection in a green frog toy acid solution made in China to 29.15 mg kg^{-1} in the acid extraction of sample 2. The adsorption of Ni by human organs my cause several health effects to lung, heart and liver and may affect the skin tissue contributing to the disease Eczema (Khan et al., 2021). These results are similar to those published by Kamara et al. (2023) for the levels of Ni in gastric solution (undetectable – 12.5 mg kg^{-1}), and close to those reported by Oyeyiola et al. (2017) (unmeasurable – 1.18 mg kg^{-1}).

Zn:-

Zinc in all explored acid extractions of toy samples was much lower than it's levels suggested by EU countries (983 mg kg^{-1}). The concentrations of Zn ranged from unmeasurable values in a yellow toy car extraction made in China to 54.93 mg kg^{-1} in multi-colour balloons acid solution imported from China.

Cd:-

Exactly 57% of examined toys contained levels of Cd in acid solutions exceeding the permissible levels for Cd set by EU by more than 4-fold. In the remainder of the toys extractions the Cd levels were not measurable.

The presence pf Cd in acid solution of children's abdomen due to swallowing pieces of coloured plastic toys may be toxic to them by affecting the liver and nervous system (Khan et al., 2021). The results of the present study are in line with that for Cd in gastric solution due to swallowing pieces of plastic toys, observed by Oyeyiola et al. (2017) (not detectable – 3.15 mg kg^{-1}) and Cui et al. (2015) (unmeasurable – 1.15 mg kg^{-1}).

Sb:-

The levels of antimony in simulated gastric fluid were lower than that allowed by EU countries (60 mg kg^{-1}) and recorded concentrations ranged from below machine detection in acid extraction from a green frog imported from China to 16.82 mg kg^{-1} in a red car acid solution manufactured in China. These findings agreed with that obtained by Cui et al. (2015) for solubility of Sb from plastic toys in stomach acid solution (unmeasurable – 0.188 mg kg^{-1}) and that reported by Astolfi et al. (2020).

Pb:-

Exactly 50% of studied acid extractions from toys contained levels of Pb exceeded Pb values recommended and set by EU countries (2 mg kg^{-1}). The concentrations of Pb in acid solution ranged from undetectable levels in the acid extraction of multi colour balloons made in China to 3.59 mg kg-1 solubilised acid fraction from a yellow car imported from China. The levels of Pb in acid fraction found in this investigation was similar to that of research conducted by Cui et al. (2015) (undetectable – 2.43 mg kg-1), but lower than that obtained by Kamara et al. (2023) (8.24 – 48.2 mg kg^{-1}).

Sn:-

The tin fraction found to migrate from studied toys to gastric solution ranged from 0.22 mg kg^{-1} in a yellow car fabricated in Egypt to 17.38 mg kg^{-1} in a red-coloured Chinese car. The concentration of Sn in gastric solution found in this study was lower than allowable levels set by EU countries (12 mg kg^{-1}) except in the extracions of sample 2 and 8 (Turner and Filella, 2021).

The presences of toxic metals in children body fluids and specifically saliva and gastric solution may be due to the use of several pigments that contain toxic metals e.g., Pb, Cd and As may lead to increase the levels of these metals in the biological liquids of human body such as saliva and gastric solution and alongside with other sources of pollution in the environment Cui et al., 2015).

Hazard Index (HI) of studied toxic elements depending on the bio-accessibility tests.

To evaluate the health risk associated with the presence of several poisonous metals in biological fluids such as saliva and gastric medium HI is used frequently. When calculated, if a HI value of more than 1 is obtained it warrants attention as a high-risk value and therefore a high health risk and should be not ignored also the range for HI is between 1 – 0.1 should be taken in account, but when its calculated value is less than 0.1 it may be ignored (Cui et al., 2015). The calculated results for HI are illustrated in table (3), and discussed as follows:

HI of poisonous studied elements in artificial saliva

The HI for metals extracted by artificial saliva calculated values less than 1 in the cause of Sb, Sn, Pb and Zn, however, the HI values > 1 in the cause of Al, Cd, and Mn alongside with Ni in 50% of studied toys and Cr in 21% of samples indicate a high heath risk to the children playing with these brands of coloured plastic toys. The HI values ranged from 1 – 0.1 in the cause of Pb in 71% of studied samples which is still a concern.

Table 3. Calculated Hazard index (HI) for extracted studied metals by artificial saliva (Sa.) and gastric solutions (0.07 M HCl).

Sample Code	Sample type	Sample Colour	Producer	Studied metals																	
				Al		Cr		Mn		Ni		Zn		Cd		Sb		Pb		Sn	
				Sa.	HCl	Sa.	HCl	Sa.	HCl	Sa.	HCl	Sa.	HCl	Sa.	HCl	Sa.	HCl	Sa.	HCl	Sa.	HCl
1	Car	Yellow	China	**2.5**	0.01	0.4	0.00	**28**	**34**	**1.58**	**1.2**	0.0004	0.000	**6.09**	**9.7**	0.015	0.017	0.24	**0.97**	0	0.002
2	Balloons	Multi colours	China	**2.2**	**0.23**	**2.2**	0.69	**30**	**16**	**2.19**	**32**	0.0002	0.199	**8.53**	**2.4**	0.009	0.007	0.30	0.00	0	0.047
3	Frog	Green	China	**6.1**	0.01	0	**2.04**	**12**	**28**	**3.53**	0.0	0.0003	0.004	0	**9.7**	0.000	0.000	0.46	**0.67**	0.01	0.002
4	Kitchen items	Orange	China	**2.2**	0.01	0	**2.23**	**15**	**30**	**19.38**	**1.2**	0.0005	0.007	**2.44**	**9.7**	0.002	0.017	0.21	0.06	0.01	0.001
5	Pokemon	Yellow	China	**2.2**	0.01	0	0	**12**	**2**	**4.75**	**6.8**	0.0007	0.004	0.49	0.0	0.001	0.004	0.18	**0.37**	0.01	0.035
6	Penguin	Blue	China	**3.9**	0.01	0.3	0	**22**	**2**	**1.95**	**3.9**	0.0013	0.004	**8.29**	0.0	0.013	0.004	0	**0.67**	0	0.039
7	Bear	White	China	**2.5**	0.01	0.3	0	**32**	**1**	**3.41**	**4.4**	0.0002	0.004	**9.75**	0.0	0.012	0.004	0.30	**0.21**	0	0.035
8	Car	Red	China	**2.5**	0.01	**1.2**	**1.19**	**36**	**26**	**2.19**	**1.2**	0.0007	0.008	**6.58**	**9.7**	0.015	0.018	0	**0.67**	0	0.063
9	Car	Blue	China	**6.3**	0.01	0	**1.54**	**12**	**27**	**12.31**	**1.2**	0.0004	0.012	0	**9.7**	0.000	0.000	0.40	**0.21**	0.01	0.002
10	Gone	Dark red	China	**2.3**	0.01	0	0.00	**15**	**2**	**11.09**	**7.4**	0.0005	0.004	0	0.0	0.001	0.004	0.46	**0.67**	0.01	0.022
11	Kitchen items	white	Egypt	**3**	0	**1.4**	0.00	**21**	**3**	**2.07**	**2.2**	0.0007	0.004	**7.56**	0.0	0.011	0.004	0.06	**0.37**	0	0.026
12	Car	Yellow	Egypt	**2.1**	0.01	0	**1.83**	**7**	**32**	**0.26**	**1.2**	0.0005	0.002	0	**9.7**	0.001	0.017	0.18	0.06	0.01	0.001
13	Car	Blue	Egypt	**2.1**	**0.23**	0	0	**8**	**10**	**10.97**	**7.6**	0.0001	0.002	0	**2.4**	0.001	0.006	0.27	**0.67**	0.01	0.039
14	Car	Pink	Egypt	**2.4**	0.01	0	0	**7**	**1**	**9.26**	**4.9**	0.0003	0.004	0	0.0	0.002	0.004	0	**0.67**	0.00	0.035

HI > 1 refers to high health risk, and should be not ignored when HI ranged between 1 – 0.1, but when it calculated value less < 0.1 may be ignored (Cui et al., 2015).

CONCLUSION

The present study investigated the bio-accessibility of Al, Cd, Cr, Mn, Ni, Pb, Sb Sn and Zn from coloured plastic toys, extracted using artificial saliva and 0.07 M HCl, simulating children's gastric solution. These toys had been imported to Libya from China and Egypt. The investigated metals can transfer from plastic toys to saliva and gastric solutions at different levels reaching recorded concentrations of Cd and Cr at higher values than those set by the EU safety bodies. Similarly, Al migrated from all samples and Cd migrated from most toys samples, both solubilised by gastric solution, again at levels greater than recommended by the EU. Additionally, the HI values showed variation among studied samples indicating a high and low health risk due to the occurrence of several target metals in coloured plastic toys. In this context, further investigations are needed to explore toxic metals concentrations and specifically heavy metals present in cheap children's toys and the associated health risk, and to protect future generations of Libyan children, proper regulations controlling the import, trade and distribution of coloured children's plastic toys is required.

LIMITATIONS

Due to the large number of samples for metal extraction (90 samples), the technician who conducted the evaluation of target metals levels in the saliva and gastric solution extraction was unable to measure all samples in triplicate. This was due to the lack of required materials for the instrument, resulting in one replicate of every sample only being analysed.

ACKNOWLEDGMENTS

The authors are extremely thankful to Ali Abdullah Own for his practical help in measuring the studied samples by XRF Spectrometer Cube, also Dr. Nerys Lloyd Mullally for editing this work.

AUTHOR CONTRIBUTIONS

Salem Irhema S. Irhema: Conceptualization, Validation, Formal analysis, Resources, Supervision of laboratory work, Data analysis, curation and writing of the original draft.

Nour ALhuday Abdalla Jumha : Laboratory work.

Heba Abdulqadir Abraheem: Laboratory work.

REFERENCES

Al-Qutob, M., Asafra, A., Nashashibi, T., & Qutob, A. A. (2014). Determination of Different Trace Heavy Metals in Children's Plastic Toys Imported to the West Bank/Palestine by ICP/MS-Environmental and Health Aspects. Journal of Environmental Protection, 05(12), 1104–1110. https://doi.org/10.4236/jep.2014.512108

Astolfi, M. L., Marconi, E., Lorini, L., Valentino, F., Silva, F., Ferreira, B. S., Canepari, S., & Majone, M. (2020). Elemental concentration and migratability in bioplastics derived from organic waste. Chemosphere, 259. https://doi.org/10.1016/j.chemosphere.2020.127472

Cui, X. Y., Li, S. W., Zhang, S. J., Fan, Y. Y., & Ma, L. Q. (2015). Toxic metals in children's toys and jewellery: Coupling bio-accessibility with risk assessment. Environmental Pollution, 200, 77–84. https://doi.org/10.1016/j.envpol.2015.01.035

Echa. (2012). Cadmium And Cadmium Compounds In Plastics Upcoming Request From The Commission For Echa To Prepare An Annex Xv Dossier: Status And Preliminary Implications Preparatory Report.

Kamara, I., Adie, G. U., & Giwa, A. S. (2023). Total and bio-accessible toxic metals in low-cost children toys sold in major markets in Ibadan, South West Nigeria. Scientific African, 20. https://doi.org/10.1016/j.sciaf.2023.e01613

Karas, K., & Frankowski, M. (2018). Analysis of hazardous elements in children toys: Multi-elemental determination by chromatography and spectrometry methods. Molecules, 23(11). https://doi.org/10.3390/molecules23113017

Karcioglu, O., Rets, A., Salgado-Bustamante, M., & Capitão, C. (2022). Exposure to heavy metals and red blood cell parameters in children: A systematic review of observational studies.

Khan Tanoli, A., Ahmed, T., & Ahmed, M. (2021). Contamination by Hazardous Elements in Low-Priced Children's Plastic Toys Bought on the local Markets of. https://doi.org/10.21203/rs.3.rs-1001076/v1

Klotz, K., Weistenhöfer, W., Neff, F., Hartwig, A., Van Thriel, C., & Drexler, H. (2017). The health effects of aluminum exposure. Deutsches Arzteblatt International, 114(39), 653–659. https://doi.org/10.3238/arztebl.2017.0653

Mračević, S. D., Ražić, S., Trišić, J., Mitrović, N., & Dukić-Ćosić, D. (2022). Toxic elements in children's crayons and colored pencils: Bio-accessibility assessment. Journal of the Serbian Chemical Society, 87(6), 723–734. https://doi.org/10.2298/JSC20091078D

Oyeyiola, A. O., Akinyemi, M. I., Chiedu, I. E., Fatunsin, O. T., & Olayinka, K. O. (2017). Statistical analyses and risk assessment of potentially toxic metals (PTMS) in children's toys. Journal of Taibah University for Science, 11(6), 842–849. https://doi.org/10.1016/j.jtusci.2017.02.005

Shahzad, L., Ali, M., Zubair, H., Sharif, F., Hayyat, M. U., & Ghafoor, G. Z. (2022a). Detection of heavy metals in children playing products and its associated health risk assessment in Lahore, Pakistan. International Journal of Environmental Analytical Chemistry. https://doi.org/10.1080/03067319.2022.2106433

Shahzad, L., Ali, M., Zubair, H., Sharif, F., Hayyat, M. U., & Ghafoor, G. Z. (2022b). Detection of heavy metals in children playing products and its associated health risk assessment in Lahore, Pakistan. International Journal of Environmental Analytical Chemistry. https://doi.org/10.1080/03067319.2022.2106433

Turner, A., & Filella, M. (2021). Hazardous metal additives in plastics and their environmental impacts. In Environment International (Vol. 156). Elsevier Ltd. https://doi.org/10.1016/j.envint.2021.106622

BURG, 2015. Aluminium-coated plastic - Metallisation of plastic components. Available at: https://burg-thermoforming.com/en/blog/aluminium-coated-plastic-metallisation-of-plastic-components. [Accessed by 31 July2024].

Fadaei, A., 2023. An investigation into the present levels of contamination in children's toys and jewelry in different countries: a systematic review. Reviews on Environmental Health, 38(4), pp.601-611. https://doi.org/10.1515/reveh-2022-0064

Irhema. S. R. S., 2006. Estimating the amount of lead in ceramic utensils manufactured in Gharyan. Master thesis in environmental sciences. Libyan Academy. Libya.

Janssen, M.P.M., Spijker, J., Lijzen, J.P.A. and Wesselink, L.G., 2016. Plastics that contain hazardous substances: recycle or incinerate?.

Wright, J. (2003). Environmental Chemistry. 1st ed. Routledge. New fetter. London. EC4P. 4EE. pp; 208 – 211. https://doi.org/10.4324/9780203414101: accessed by 23/9/2024

Weidenhamer, J.D. and Clement, M.L., 2007a. Widespread lead contamination of imported low-cost jewelry in the US. Chemosphere, 67(5), pp.961-965. https://doi.org/10.1016/j.chemosphere.2006.10.07. accessed by 25/9/2024