

## RESEARCH PAPER

# Estimation of Some Metals in Children's Colorful Modeling Clay Sold in the Markets of Erbil City, Kurdistan Region, Iraq

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### ABSTRACT:

Toxic heavy metals are commonly introduced in the manufacturing of various children's products. In this study, nine different types of modeling clay brands collected from several markets in Erbil city were analyzed to assess the content of heavy metals including Cd, Cr, Cu, and Ni. The metals analyses were performed on different colors available in each of the purchased brands. Strong acids such as nitric acid (HNO<sub>3</sub> 65%), and perchloric acid (HClO<sub>4</sub> 70%) were performed to digest samples. Concentrations of the selected metals were determined using a flame atomic absorption spectrophotometer (FAAS). Data showed that numbers of examined clays samples detected with Cr, Cd Cu, and Ni metals were 0, 5, 36, and 40 out of 54 examined clay samples, respectively. Ni and Cu were found in varying concentrations in most (detected in 8 brands out of 9 collected clay brands) of the examined clay brand samples. The total of the detected metals load in the nine analysed brands were as follows; Chinese-3 (221.41 mg/kg) > Italian (75.84 mg/kg) > Chinese-4 (68.00 mg/kg) > German (61.31 mg/kg) > Chinese-6 (58.67 mg/kg) > Turkish (54.05 mg/kg) > Chinese-5 (52.51 mg/kg) > Chinese-1 (23.7 mg/kg) > Chinese-2 (23.31 mg/kg). Data confirms that the concentrations of the selected metals in whole examined samples were below European Union permissible limits (EN 71-3:2013, Category-I) for the migratable metals in pliable clay toys except one clay sample (819.2 mg/kg of Cu in blue clay color). An analysis of variance (ANOVA) was applied to find the presence of significant differences among analysed brands of modeling clay samples.

KEY WORDS: AAS, Children toy, Heavy metals, Modeling Clay

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## 1. INTRODUCTION

A toy is defined as any designed essential product for children's growth and development. Plying more time with toys by children is a great habit and has a vital role in a child's development (Kumar and Pastore, 2007, ISO, 8124-1. 2014). The most commonly used material to made soft children toys is polyvinyl chloride (PVC) which includes several additives.

Heavy metals and their compound are present and widely used from manufacturing children's toys as the necessary flexibility, stability, catalysts, coloring agents, brightness, softness, and many other additives (Belliveau and Lester, 2004, Guney and Zagury, 2012, Sindiku and Osibanjo, 2011). Cadmium and lead act as a stabilizer in toys and are also used in pigments to improve the attraction of toys visualization. Recent studies showed that both PVC and non-PVC children's toys included different concentrations of metals. Heavy metals are naturally 5 times denser than

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water and cannot be metabolized by the body (Cui et al., 2015, Hillyer et al., 2014, Oyeyiola et al., 2017).

Due to beginning of industrialization, heavy metals have become a major health problem and observed in food, water, air, soils, drugs, plants, cosmetics, plastic toys, cookware, and other daily household tools (Kumar and Pastore, 2007, Kumar Das et al., 2011, Sindiku and Osibanjo, 2011, Abdullah et al., 2017, Amin et al., 2017, Darwesh, 2019, Bazzaz and Muhammad, 2018, Abd-Alhameed, 2019). In developing countries like China, it is known the rising number of children at risk for toxic heavy metals' exposure. It was revealed that the increased risk of several behavioural problems like anxiety, somatic complaints, withdrawn, thought problems, social problems, attention problems, delinquent and aggressive for school-aged children was associated with a polluted area with heavy metals' exposure (Bao et al., 2009). Heavy metals can cause unacceptable significant hazard risks and major disruption function problems in the human mental, nervous system, lungs, kidneys, and other organs (Duffus, 2002, Martin and Griswold, 2009).

Chemical exposure to children, especially leaching toxic heavy metals from plastic toys and painted materials, is an emerging concern. Child behaviours with plastic toys like stretching, chewing, sucking, licking, and swallowing can be seen as common and the impact source of heavy metal exposure due to leaching out toys component (Kumar and Pastore, 2007).

Exposure to a high concentration of heavy metals including cadmium (Cd), lead (Pb), chromium (Cr), nickel (Ni) and copper (Cu) can have several harmful health effects and problems (Cui et al., 2015, Martin and Griswold, 2009). Cadmium exposure at contents present in most countries can be harmful to early life and have an impact on child brain development (Kippler et al., 2012). It is also recognized to damage many organ functions, and increase cancer risk (Järup and Åkesson, 2009).

Even with the deserve attention and regulation of heavy metal contamination in children's toys, recent studies declared that more precaution is

required through the production of children's toys and to limit the importing and handling of such child products into the markets. (Al-Qutob et al., 2014, Guney and Zagury, 2012, Ismail et al., 2017, Issa and Alshatteri, 2019). Varying concentrations of Cd and Pb and other toxic elements were recorded in several unbranded Indian soft plastic toys (Kumar and Pastore, 2007), 20 toys and children's jewellery bought on the North American market (Guney and Zagury, 2013), thirty different soft plastic toys collected from the Ghanaian markets (Kudjoe Gati et al., 2014), and over 100 of the collected vintage plastic toys (Miller and Harris, 2015). These toxic metals were recently detected in several PVC and non-PVC plastic toys (Oyeyiola et al., 2017) 200 second-hand plastic toys sourced in the UK (Turner, 2018), and different toy samples in Poznań city (Poland) (Karaś and Frankowski, 2018) and six infant care plastic products sold in markets of Kalar City, Kurdistan Region, Iraq (Issa and Alshatteri, 2019).

The Scientific Committee on Health and Environmental Risks (SCHER) mentioned that the average ingested daily intake toy materials are still appropriate as follows; 400 mg/d for liquid or sticky toy material, 100 mg/d for dry, brittle, powder-like or pliable toy material, and 8 mg/d for scraped-off toy material (EC, SCHER, 2016). However, in a worst-case assessment, ingestion values of different toy materials were found above permission standard limits for several toy products. Results confirmed that 739 and 151.8 mg/d average value were recorded as total ingested daily intake toys for liquid or sticky and dry, brittle, powder-like or pliable toy material, respectively (Danish, EPA, 2014).

Several methods for the assessment of bio-availability and Hazard Index (HI) with health risk characterization were recently recommended and applied to investigate metals health hazard exposure in various products of children's toys (Cui et al., 2015, Dahab et al., 2016, Guney et al., 2014, Guney and Zagury, 2014b, Oyeyiola et al., 2017). Last decades, scientists and physicians have extremely mentioned that no content of Cd or Pb metal in human blood is normal or considered harmless. They emphasized that what was 'safe' yesterday is no longer 'safe' today or tomorrow. Thus, the present 'safe' limits of heavy metals have been revised in blood, baby toys and

environments samples due to continuing scientific studies (Kudjoe Gati et al., 2014, Kumar and Pastore, 2007).

There is only one recent local study on the assessment of element contents in infant care plastic products sold in markets of Kalar City, Kurdistan Region, Iraq. The detected metals ranges for Cd, Cr, Cu, and Ni in six samples were (not detectable (ND)-0.10 mg/kg), (ND-71.12 mg/kg), (0.127-17.3 mg/kg), and (0.004-2.15 mg/kg) respectively. The detected contents of whole analyzed metals were lower than the world permissible limits while Cr contents were exceeded the permissible limit in most of the analysed samples (Issa and Alshatteri, 2019). However, few studies are available and have been recently examined for the assessment of heavy metals in colorful baby clay. According to the investigated study in Lebanon, inexpensive modeling clay is popular, and there is not good legislation to regulate such toys. The community survey declared that only 17 % of families in Lebanon were attentive to the health hazard of such toys and 82 % of parents try to purchase

inexpensive and unbranded toys for their children (Korfali et al., 2013). Erbas et al. (2017) stated that the recorded contents (mg/kg) range of some metals in nine play dough samples were ND for Co, ND – 4.8 for Pb, 0.14 – 1.2 for Cd, 1.2 – 3.9 for Ni, 0.8 – 6.6 for Mn, and ND – 219 for Cu. Sogut and Ezer (2017) also reported that 13 different brands of children's play dough samples marketed in Turkey were investigated to determine elemental composition. The contents (mean±SD) of the analysed some elements were ND for Cd,  $1.59 \pm 0.76$  mg/kg for Hg,  $4.08 \pm 1.89$  mg/kg for As,  $17.21 \pm 18.43$  mg/kg for Pb,  $32.20 \pm 19.44$  mg/kg for Mn,  $53.60 \pm 16.72$  mg/kg for Cu, and  $63.16 \pm 29.03$  mg/kg for Zn.

In recent times, the maximum permissible content of migrated heavy metals in children toys have been regulated, declared and updated by many jurisdiction standards (Table 1) including European Union New Toy Safety Directive (EN, 71-3: 2006), European Toys Safety Directive (EC, 2009), International Standard (ISO, 8124-3. 2010), and European Union (EU) New Toy Safety Directive (EN, 71-3: 2013).

**Table 1:** Showing the country world permissible limits of migrated heavy metals (mg/kg) from children toy

Standards Jurisdiction	Scope	Maximum acceptable metals migration from toy materials (mg/kg)				
		Cu	Ni	Cd	Cr (III)	Cr (VI)
European Union (EN, 71-3: 2006)	For modeling clay and finger paints	--	--	50	25	--
European Union 2009/48/EC (EC, 2009)	Category I	622.5	75	1.9	37.5	0.02
	Category II	156	18.8	0.5	9.4	0.005
	Category III	7700	930	23	460	0.2
International Standard (ISO, 8124-3. 2010)	Any toy material given in clause I, except modeling clay and finger paint	--	--	75	60	--
	Modeling clay and finger paint	--	--	50	25	--
European Union (EN, 71-3: 2013)	<b>Category I</b>	<b>622.5</b>	<b>75</b>	<b>1.3</b>	<b>37.5</b>	<b>0.02</b>
	Category II	156	18.8	0.3	9.4	0.005
	Category III	7700	930	17	460	0.2

Category I: in dry, brittle, pliable or powder-like toy material, Category II: in liquid or sticky toy material, Category III: In scraped-off toy materials.

Toys and modeling clay must be safe and are essential for children's growth and development. To the best of our knowledge, there is no previous study addressed the amount contents of heavy metals in children modeling clay marketed in Erbil city/Iraq country. Thus, the main aim of this study was to evaluate the content of selected heavy metals in different brand samples of

colorful modeling pliable clay collected in the markets of Erbil city. To know toys' product safety, the content of analysed metals can be compared with the recent international permissible limits (Category-I) for metals (EN, 71-3: 2013) due to none availability of the updated Iraqi standards for heavy metals in toys.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

Different chemicals including nitric acid ( $\text{HNO}_3$  65%), and perchloric acid ( $\text{HClO}_4$  70%) were used with analytical grade throughout the experiment study for sample digestion. According to AAS manufacturer guideline (Whiteside and Milner, 1984), chromium nitrate [ $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ] and nickel nitrate [ $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ] were used and dissolved in distilled water throughout the experiments for the preparation of 1000 mg/kg of Cr and Ni stock solutions respectively. Chemicals such as CdO (dissolved in 5M diluted HCl) and Cu metal (dissolved in 5M  $\text{HNO}_3$ ) were also used to prepare 1000 mg/kg of Cd and Cu stock solutions respectively. Then, serious working solutions for the selected of the metals ion were individually prepared from the stock solutions according to the instruments manufacturer guideline (Whiteside and Milner, 1984).

### 2.2. Instrumentation

Flame atomic absorption spectrometer (FAAS) (Pye-Unicam SP9 model flame AAS, Cambridge, CB, UK) accoutered with a hollow cathode lamp as the light source and acetylene-air flame burner was used to determine selected metal ions in whole sample solutions. The instrumental parameters and optimum conditions were those suggested by the manufacturer guideline (Whiteside and Milner, 1984). The wavelengths (nm) selected for the determination of the metals ion were as follows: Cd, 228.8 nm; Ni, 232.0 nm; Cu, 324.8 nm and Cr, 357.9 nm. Acetylene ( $\text{C}_2\text{H}_2$ ) flow rate was 0.8-1.4  $\text{mL min}^{-1}$  and air flow rate was 18-28  $\text{mL min}^{-1}$ . The nebulizer uptake rate was 6  $\text{mL min}^{-1}$ . The hallow cathode lamp currents were 5, 8, 12, and 15 mA for Cu, Cd, Cr, and Ni respectively.

### 2.3. Sample collection

During sampling, nine different brands of children modeling clay samples were obtained from local markets in Erbil city, Kurdistan Region (Iraq) during January 2018. The obtained samples were collected based on different brands name and

origins. The collected samples included the following nine brand names (code); Glotto (Italian), Lyra (German), Lets Have Fun (Turkish), Play Doh (Chinese-1), 5D Mini Normal (Chinese-2), and 5D-Mini Soft (Chinese-3), Modeling Clay (Chinese-4), Play Dough (Chinese-5), and Tong Tong (Chinese-6). Seven main colorful clay samples for each of the collected brands were available except the Italian and German made brands.

### 2.4. Sample preparation and digestion for analysis

Sample digestion for metal analysis was carried out according to the published methods (Guney and Zagury, 2014b, Guney and Zagury, 2014a). Prior to analysis, digestion 1.0 g of a modeling clay sample was quantitatively subjected to strong wet acid digestion using nitric acid ( $\text{HNO}_3$  65%) on digestion-heater, followed by perchloric acid ( $\text{HClO}_4$  70%). At first, a volume of 15 ml of concentrated  $\text{HNO}_3$  was used to destruct the sample on digestion-heater until the brown fumes were appeared and liberated at about 150°C temperature. After cooling, 5 ml of concentrated  $\text{HClO}_4$  then was added to complete digestion until the white vapors of the acid were liberated (Figure 1). The digested sample solution was cooled, quantitatively transferred and then diluted into a 50 ml volumetric flask with distilled water. Finally, the last solution was labelled and stored until the final analysis and analyzed directly without any further dilution with distilled water. The above steps were repeated for blanks and each of the seven colors individually for each collected brand samples. Solution which contains only the digested acids or the reagents used to dissolve or digest the analyzed samples were individually prepared, used as blank and repeated three times for each of samples and working solutions. Blank solution is mainly used for calibration purposes or zeroed the absorbance of all the other presented components in the sample solution except the component of interest.



**Figure (1):** Wet digestion of the clay samples; (a) liberating brown fumes after addition concentrated  $\text{HNO}_3$ , (b) liberating white fumes after addition concentrated  $\text{HClO}_4$

### 2.5. Sample analysis

Flame atomic absorption spectrometer (FAAS) was used and applied to determine the concentration of the selected heavy metals; chromium (Cr), nickel (Ni), copper (Cu), and cadmium (Cd) in seven main color clay samples from the collected brands. During analysis, some of the digested solutions were further diluted with distilled water when (necessary) concentration of analyzed metals in the sample solution was higher than the used metal linear range. Results were determined in mg/L (parts per million) in whole the digested solutions and converted into mg/Kg to find the contents of the selected metals in each of the colorful clay samples using dilution factor equation (Equation 1) as follows:

$$\text{mg/Kg} = \frac{(\text{mg/L}) \times 50.0 \text{ mL}}{\text{accurate mass of 1.0 g sample}} \dots (\text{Eq. 1})$$

Results data were then used for the statistical data analysis.

### 2.6. Statistical analysis

This research was performed on nine different collected brands of modeling clay samples which included seven main colors for each brand. Several colors were selected for each brand to show the differences of the detected metal contents as heavy metals are broadly used in the manufacture of several industrial products such as colour pigment in paints (Järup, 2003). The results of this study were analyzed for statistical

comparison using GraphPad Prism 6 and Microsoft Excel 2010 program software. An analysis of variance ANOVA was applied to assess differences in the mean concentration of the analyzed metals in modeling clay products. Data in tables and figures are shown in tabulated form as mean  $\pm$  standard deviations (SD) and not detectable (ND) or below detection limit.

### 3. RESULTS AND DISCUSSIONS

The whole number of analyzed modeling clay brand was nine with different colors and brands. Seven main colors including white (W), black (Bk), yellow (Y), green (G), blue (B), red (R), and mixture (M) were available for each of the analyzed brands excepting the Italian and German made brands with few colors. Most of the available and selected brands were Chinese made. An adequate analytical estimation test was performed for assessment and finding the concentration of four heavy metals including chromium, nickel, copper, and cadmium in 54 examined colorful clay samples for the seven selected brands.

Detailed information including brands name, origin, color and the recorded metals content of the analyzed modeling clays are shown in Table 2. The finding results in the table confirms that Cr, Cd, Cu and Ni metals were presented and detected in 0, 5, 36, and 40 samples out of 54 examined colorful clay samples respectively. Both Cu and

Ni metals were recorded with a high amount in most of the 54 examined pliable colorful clay samples (Figure 2 and 3).

Columns diagram of the nickel and copper metal content in the entire main examined color including white, black, yellow, green, blue, red, and mixture color are individually illustrated for each of the collected brands in the Figure 2 and Figure 3, respectively. Figure 2 verifies that nickel

metal was observed in at least five tested color available from each of the Turkish, Chinese-1, Chinese-3, Chinese-4, and Chinese-5 made brands. Based on ordering detected metals content in each pliable color, Cu metal was presented and recorded as the highest value in all the examined blue color clay followed by green color for each of the investigated brands excepting the Italian and German made brands (Figure 3).

**Table 2:** Concentration (mg/kg) of analyzed metals based on different colors modeling clay (n =2)

(Origin) Brand name	Code	Metal	Content of analyzed metals as ppm (mg/kg) in vary colorful modeling clay							
			(W)	(Bk)	(Y)	(G)	(B)	(R)	(M)	Mean±SD
(Italy) Glotto	Italian	Cu	40.6	NA	NA	NA	NA	25.00	25.00	30.20±9.00
		Cd	ND	NA	NA	NA	NA	ND	0.87	0.29±0.50
		Cr	ND	NA	NA	NA	NA	ND	ND	ND
		Ni	48.77	NA	NA	NA	NA	40.57	46.72	45.35±4.30
(Germany) Lyra	German	Cu	NA	NA	NA	NA	NA	ND	ND	ND
		Cd	NA	NA	NA	NA	NA	0.21	0.21	0.21±0.0
		Cr	NA	NA	NA	NA	NA	ND	ND	ND
		Ni	NA	NA	NA	NA	NA	61.10	61.10	61.10±0.0
(Turkey) Let's Have fun	Turkish	Cu	37.98	ND	37.98	47.59	62.01	35.57	36.77	36.84±18.80
		Cd	ND	ND	ND	ND	ND	ND	ND	ND
		Cr	ND	ND	ND	ND	ND	ND	ND	ND
		Ni	24.18	ND	15.98	15.98	24.18	20.08	20.08	17.21±8.30
(China) Play Doh	Chinese-1	Cu	ND	30.76	33.17	33.17	35.57	ND	33.20	23.70±16.20
		Cd	ND	ND	ND	ND	ND	ND	ND	ND
		Cr	ND	ND	ND	ND	ND	ND	ND	ND
		Ni	ND	ND	ND	ND	ND	ND	ND	ND
(China) 5D Mini Normal	Chinese-2	Cu	ND	ND	ND	ND	66.82	ND	ND	9.55±25.30
		Cd	ND	ND	ND	ND	ND	ND	ND	ND
		Cr	ND	ND	ND	ND	ND	ND	ND	ND
		Ni	ND	15.98	15.98	20.08	ND	28.28	15.98	13.76±10.40
(China) 5D Mini Soft	Chinese-3	Cu	ND	25.00	35.60	319.20	<b>819.20</b>	ND	230.2	204.2±298.9
		Cd	ND	ND	ND	ND	ND	ND	ND	ND
		Cr	ND	ND	ND	ND	ND	ND	ND	ND
		Ni	20.08	15.98	24.18	20.08	15.98	ND	24.18	17.21±8.3
(China) Modeling Clay	Chinese-4	Cu	30.76	37.98	ND	62.01	95.67	ND	30.76	36.74±33.9
		Cd	ND	ND	ND	ND	ND	0.21	0.20	0.06±0.1
		Cr	ND	ND	ND	ND	ND	ND	ND	ND
		Ni	32.38	36.47	28.28	36.47	32.38	15.98	36.47	31.20±7.37
(China) Play Dough	Chinese-5	Cu	35.57	35.57	33.17	40.38	66.82	35.00	42.78	41.33±11.70
		Cd	ND	ND	ND	ND	ND	ND	ND	ND

		Cr	ND							
		Ni	ND	15.98	ND	ND	15.98	15.98	30.33	11.18±11.60
<b>(Chine) Tong Tong</b>	<b>Chinese-6</b>	Cu	40.38	ND	ND	37.98	57.21	ND	42.78	25.48±24.60
		Cd	ND							
		Cr	ND							
		Ni	44.67	28.28	32.38	32.38	28.28	24.18	42.62	33.19±7.56

ND: Not Detectable, NA: Not Available, SD: Standard Deviation, W: White color, Bk: Black color, Y: Yellow color, G: Green color, B: Blue color, R: Red color, M: Mixture color, n: the sample repetition

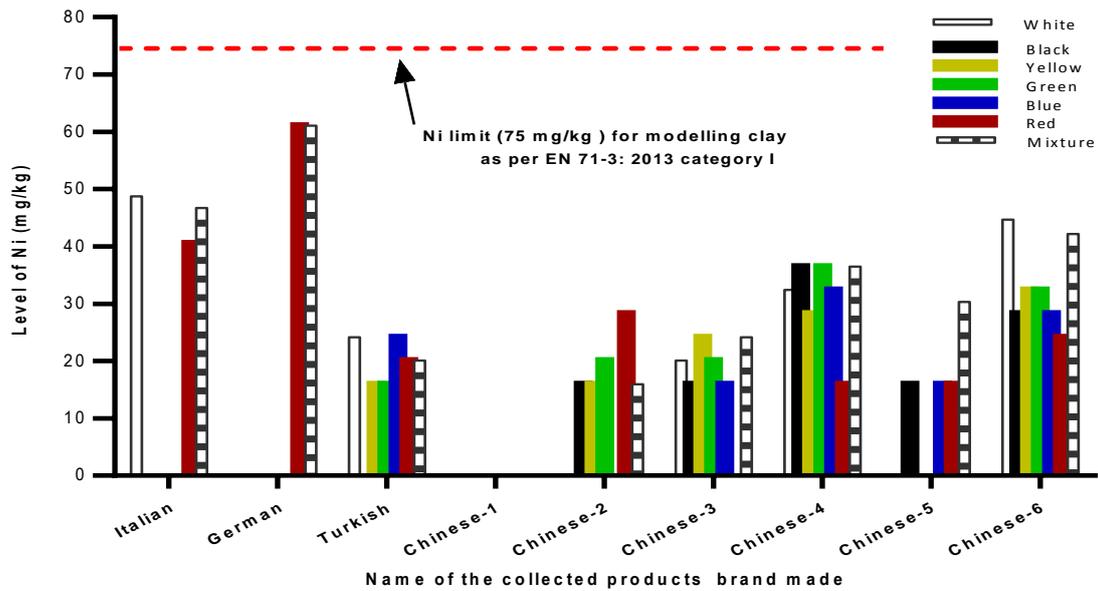


Figure (2) Concentration of nickel in the seven modeling clay colors collected from nine brands

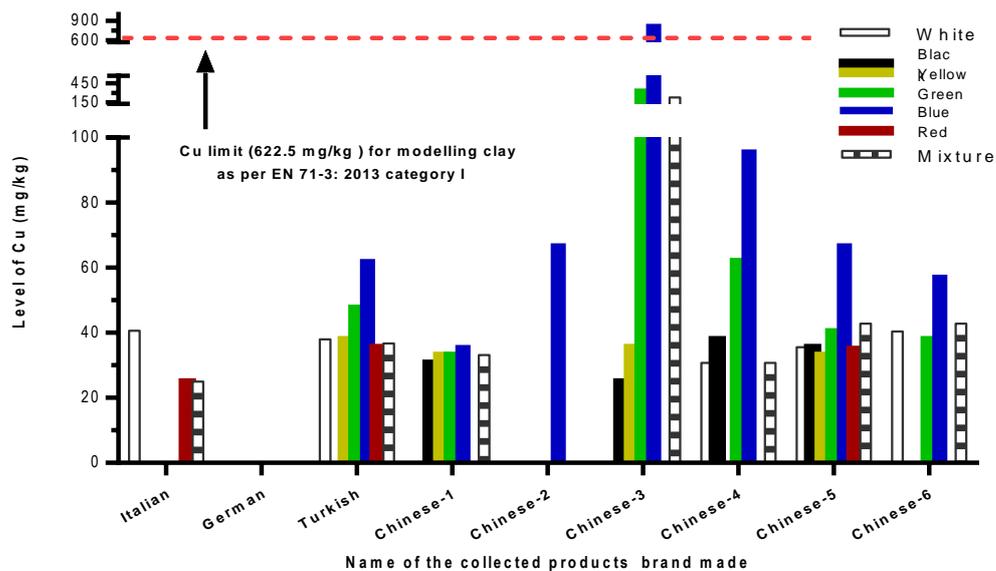


Figure (3) Concentration of copper in the different colorful modeling clay collected from nine brands

The summarized results of heavy metal concentration, the mean, range, standard deviation (SD), the available number of colorful samples per brands, number of samples detected with metals and a total of the detected metals load are presented in Table 3. Results show that the copper content ranged between ND - 819.2 mg/kg, while the nickel content ranged from ND - 61.10 mg/kg in different modeling clay. In addition, cadmium concentrations were only detected in 5 samples out of the whole (54) tested samples. The contents of the Cd metal in most of the chosen colorful clay sample were presented as non-detectable except the Italian (0.87 mg/kg in mixed color), German (0.21 mg/kg in red and mixture color), and Chinese-4 (0.21 mg/kg in red and 0.20 mg/kg in mixed color) brands. However, the total chromium concentration including Cr(III) and Cr(VI) was not detectable and also below the detection limit in the entire of the examined samples. Chromium's speciation which is Cr(III) and Cr(VI) was not performed and not identified in this study.

The total of the detected metals load in the entire nine analysed brands were recorded and ordered as follows in Table 3; Chinese-3 (221.41 mg/kg) > Italian (75.84 mg/kg) > Chinese-4 (68.00 mg/kg) > German (61.31 mg/kg) > Chinese-6 (58.67 mg/kg) > Turkish (54.05 mg/kg) > Chinese-5

(52.51 mg/kg) > Chinese-1 (23.7 mg/kg) > Chinese-2 (23.31 mg/kg).

Health risks of pliable clay can pose higher than usual children plastic toys because it is clear that modeling clay can be easily mouthed and chewed by children. Modeling clay toy relates to Category I which includes dry, brittle, pliable or powder-like materials that caused to leave a residue or trace on humans hands. Therefore, the permissible migration limits of toxic heavy metals in modeling clay (Category-I) were cautiously regulated to be stricter than those set for Child products including Category-III (scraped-off materials) (EN, 71-3: 2006, EN, 71-3: 2013). This is owing to the fact that brittle or pliable clay characterize a special toy category where the ingestion of higher amounts of these toy materials is imaginable during an exposure. Data for the selected metals concentrations in this study were evaluated and compared with recently standard permissible limits which regulated and highlighted by European Union (EU) New Toy Safety Directive (EN, 71-3: 2013) to stipulate the maximum permissible values of metals such as cadmium, lead, nickel and copper in toys. The permissible amounts are the boundary assessment between safety and danger for child products and must be below the content which could be harmful to children.

**Table 3:** Summarized metals content recorded in the vary colorful modeling clay from different brands

(n=2)

Brands Name (Code)	Metals	Metals content (mg/kg)				No. of colorful samples /brand	color samples detected with metals	Total of the detected metals load /brand (mg/kg)
		Mini.	Max.	Mean	±SD			
Glotto (Italian)	Cu	25.00	40.60	30.20	9.00	3	W, R, M	75.84
	Cd	ND	0.87	0.29	0.50	3	M	
	Cr	ND	ND	ND	ND	3	None	
	Ni	40.57	48.77	45.35	4.27	3	W, R, M	
Lyra (German)	Cu	ND	ND	ND	ND	2	None	61.31
	Cd	0.21	0.21	0.21	0.00	2	R, M	
	Cr	ND	ND	ND	ND	2	None	
	Ni	61.10	61.10	61.10	0.00	2	R, M	
Let's Have fun (Turkish)	Cu	35.57	62.01	36.84	18.80	7	W, Y, G, B, R, M	54.05
	Cd	ND	ND	ND	ND	7	None	
	Cr	ND	ND	ND	ND	7	None	
	Ni	15.98	24.18	17.21	8.30	7	W, Y, G, B, R, M	
Play Doh	Cu	30.76	35.57	23.70	16.20	7	Bl, Y, G, B, M	23.70

<b>(Chinese-1)</b>	Cd	ND	ND	ND	ND	7	None	23.31	
	Cr	ND	ND	ND	ND	7	None		
	Ni	ND	ND	ND	ND	7	None		
<b>5D Mini Normal</b>	Cu	ND	66.82	9.55	25.30	7	B		
	Cd	ND	ND	ND	ND	7	None		
	Cr	ND	ND	ND	ND	7	None		
<b>(Chinese-2)</b>	Ni	15.98	28.28	13.76	10.40	7	Bl, Y, G, R, M		
<b>5D mini soft</b>	Cu	25.00	<b>819.20</b>	204.20	298.90	7	Bl, Y, G, B, M		221.41
	Cd	ND	ND	ND	ND	7	None		
	Cr	ND	ND	ND	ND	7	None		
<b>(Chinese-3)</b>	Ni	15.98	24.18	17.21	8.30	7	W, Bl, Y, G, B, M		
<b>Modeling Clay</b>	Cu	30.76	95.67	36.74	33.90	7	W, Bl, G, B, M	68.00	
	Cd	0.20	0.21	0.06	0.10	7	R, M		
	Cr	ND	ND	ND	ND	7	None		
<b>(Chinese-4)</b>	Ni	15.98	36.47	31.20	7.37	7	W,Bl,Y,G,B,R, M		
<b>Play Doh</b>	Cu	33.17	66.82	41.33	11.70	7	W, Bl, Y, G, B, R, M	52.51	
	Cd	ND	ND	ND	ND	7	None		
	Cr	ND	ND	ND	ND	7	None		
<b>(Chinese-5)</b>	Ni	15.98	30.33	11.18	11.60	7	Bl, B, R, M		
<b>Tong Tong</b>	Cu	37.98	57.21	25.48	24.60	7	W, G, B, M	58.67	
	Cd	ND	ND	ND	ND	7	None		
	Cr	ND	ND	ND	ND	7	None		
<b>(Chinese-6)</b>	Ni	28.28	44.67	33.19	7.56	7	W, Bl, Y, G, B, R, M		

ND: Not Detectable, NA: Not Available, SD: Standard Deviation, W: White color, Bk: Black color, Y: Yellow color, G: Green color, B: Blue color, R: Red color, M: Mixture color, n: the sample repetition

The data in this study proved that the detected concentrations of the investigated metals in all (54) of the analyzed colorful modeling clay samples were below the EU permissible limits for migrated metals (622.5 mg/kg for Cu, 75 mg/kg for Ni, 37.5 mg/kg for Cr (III), 0.02 mg/kg for Cr (VI), and 1.3 mg/kg for Cd) in pliable clay toys excepting one out of 54 examined colorful clay samples (blue color in Chinese-3 made brand). High content of copper (819.2 mg/kg) in blue color clay available in 5D Mini Soft product was detected in the Chinese-3 made brand and exceeded the permissible limit for copper. In this study, there is only one examined colorful sample which exceeded EN 71-3:2013 Category-I permissible limit for migrated Cu (622.5 mg/kg) metal in dry pliable children toys (EN, 71-3: 2013).

In Chinese-3 brand, the recorded Cu contents in analyzed mixture (230.20 mg/kg), green (319.20 mg/kg), and blue (819.20 mg/kg) color samples were largely higher than the detected Cu contents in white (ND), red (ND), black (25.00 mg/kg) and yellow (35.60 mg/kg) clay samples. In Chinese-4 brand, high concentrations of Cu were also detected in blue (95.67 mg/kg) and green (62.01 mg/kg) clay color samples (Table 2 & Figure 3).

However, the highest Ni contents were detected in Chinese-6 (44.67 mg/kg), Italian (48.77 mg/kg) and German (61.10 mg/kg) brands (Table 2 & Figure 2). The presence of high contents of heavy metals could come from the used pigments from manufacturing children's toys as the necessary of coloring agents. Heavy metals which are known as the most polluting chemicals in the environment have been commonly encountered and used in paints component as pigments (Järup, 2003) and recorded with a high amount in various paint samples (Ogilo et al., 2017, Kameti, 2013, Apanpa-Qasim et al., 2016). The data of the metals mean in the Table 3 confirms that copper and nickel were detected in varying concentrations in most (8 out of 9) examined brand clay samples. It confirms that in most of the analyzed samples, the detected concentrations of Cu and Ni were higher than those in previously published studies on modeling clay (Guney and Zagury, 2013, Korfali et al., 2013).

An analysis of variance (ANOVA) two-factor without replications using a 95 % confidence level was also applied to find the presence of significant differences among whole analyzed brands of modeling clay samples in this study because the used data were the contents of the selected metals

mean (Table 3). The data of ANOVA showed that there is no statistically significant difference ( $p$ -value  $> 0.05$ ) among means concentrations for seven examined clay brands including Turkish, Chinese-1, Chinese-2, Chinese-3, Chinese-4, Chinese-5, and Chinese-6 brands.  $P$ -value,  $F$  value, and  $F_{(critical)}$  values were equal to 0.057, 3.14, and 3.287 respectively. However, both German and Italian clay brands were excluded in the ANOVA statistical analysis due to available few colors (white, red and mixture) modeling clay in these brands.

There are few studies for the assessment of heavy metals in colorful modeling clay. Korfali *et al.* (2013) investigated concentrations of some toxic metals in 23 different Far East colorful modeling baby clay toys of four brands imported into Lebanon. Korfali *et al.* (2013) reported that the recorded means  $\pm$ SD (range) contents were  $40.2\pm 45$  (ND–162) mg/kg for copper,  $9.1\pm 7$  (ND–23) mg/kg for cadmium,  $6.0\pm 5.6$  (ND–22) mg/kg for chromium, and  $6.4\pm 10.5$  (ND–15) mg/kg for nickel in the analyzed clay samples. In a worst-case assessment, more than 15 (65%) of the analyzed clay samples recorded with a high amount of cadmium ( $9.1\pm 7$  mg/kg) and exceeded the Category-I permission limit for migration Cd metal (1.3 mg/kg) in children clay toys. However, each of Cu, and Ni content was far lower than the world permission level and also finding results in this study. Furthermore, Guney and Zagury (2013) also analysed the contents of several toxic metals in 18 different brittle or pliable clay toys. Results confirmed that only 1 ( $2.81\pm 10$  mg/kg of Cd) out of 18 brittle or pliable clay samples exceeded Category-I permission limits.

According to recent study by Erbas *et al.* (2017), the detected contents of Pb, Cd, Ni, Mn, Co and Cu metals in nine examined play dough samples were below the European Union permissible limits for the migratable metals in pliable clay toys excepting one sample. Data showed that high content of Pb metal ( $4.8\pm 0.8$  mg/kg) was detected in one of the examined green clay samples which was exceeded the permissible limit (3.4 mg/kg for Pb). Sogut and Ezer (2017) also reported that various concentrations of As, Hg and Pb toxic elements were detected in the same four play dough samples out of 13 examined samples marketed in Turkey while no Cd was determined in any of the analyzed samples. The recorded

contents [mean $\pm$  S.D. (detected in number of samples)] for As and Pb were  $4.08\pm 1.89$  mg/kg (5) and  $17.21\pm 18.43$  mg/kg (8) and exceeded the recent EU permissible limits for the migratable metals. However, the detected contents for Cd and Cu were ND mg/kg (13) and  $53.60\pm 16.72$  (12) and presented with good agreement with the recorded results in the present study.

In this study, the measured contents of selected heavy metals were generally low or below the world permissible limits (Category-I), modeling clay toys could still be harmful to children due to ingesting a high amount of modeling clay toys by children in a specific case. In addition, some toxic elements such as lead, mercury and arsenic remained, could be focused and analyzed to prove the safety of available clay toy in our country. These elements can cause several chronic health risks including pertaining to the central nervous system, the gastrointestinal tract (Markowitz, 2000), neurotoxic effects (Tolins *et al.*, 2014), and acute and chronic intoxication at low levels of exposure (Bose-O'Reilly *et al.*, 2010).

#### 4. CONCLUSIONS

This study revealed that copper and nickel metal were detected in varying concentrations in most of the analyzed brand samples collected in Erbil city markets. In all cases the concentrations of copper in blue and green clay color is higher than that of copper in other colors. The recorded metal concentrations were below the permission limits except 1 out of 54 colorful pliable clay samples exceeded Category-I permission limit for copper.

#### 5. RECOMMENDATIONS

Children product toys frequently contain varying amounts of toxic heavy metals. It is recommended that there should be continuous monitoring of all children products in the local markets.

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