Lead, Nickel and Cadmium in the coating of children's toys effects and influencing factors

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Abstract. The paint covering the toy contains a high percentage of heavy metal, which is a cumulatively toxic source despite the limitations set by organizations such as WHO standard. This study is concerned about measuring the amount of Lead, Cadmium, and Nickel in the children's toys. Thirty-two samples of plastic toys were collected, in different colors i.e. black, red, and yellow that are used for all age groups 3-12 months, 1-3 years and finally 3-6 years. The samples were analyzed using SPSS program. From the results it was found that the concentration of Lead between (8.0625 - 12.1875 mg / kg), Nickel (7.125 - 12.8125 mg / kg), and Cadmium, (2.96875 -4.0625 mg / kg), provided that all results were lower from that recommended by the standard of (ISO-8124-3) and US EPA. The black color toys have high concentration of heavy metal, from the SPSS program analysis show high correlation between concentration of heavy metal with different parameter, except the correlation between lead with prices and Nickel with color.

Key words:
Children's toys coating, coating colors, different age toys, lead; nickel; and cadmium.

1. Introduction

Direct or indirect pollution with heavy metals originated from human activities mostly from industry and urbanization (Jern, 2006). These metals are usually added to a wide variety of plastic toys, in order to provide the necessary stability, and to impart some characteristics such as softness, brightness, and flexibility to those products. Children played with toys exposed to chemical contamination easily, whom they chew, lick and / or swallow their plastic as a common source of exposure to heavy metals (Sindiku, 2011: Kumar, 2007). These heavy metals Lead (Pb), Cadmium (Cd) and Nickel (Ni) have a number of risks to humans. These metals may cause chronic diseases such as breast cancer, mental retardation and reproductive health problems (Lester, 2004). Various regulatory agencies have set limits on the content of the elements in the various Toys. The European Standard for Peace of Play, EN 71, and Part 3 is in one section entitled "Migration of Certain Elements". In this section, the standard has specified the concentration limits of Lead (Pb), Nickel (Ni) and Cadmium (Cd) as 90, 25 and 75 mg / kg, respectively in paging of playing materials (European standards toys, 1995). (TSE) (TS 5219 EN 71 3 April 1997). Analysis the heavy metals in toys are done as preventive act for play safety, in the developed countries...
such as the United States. There has been widespread public anger, in the well-developed countries over the fact that plastic toys contain a large amount of heavy metals. Metal introduced 20 million Chinese-made toys on 14 Aug. 2007 (Allen, 2008: Consumer Federation of America, 2008), in the international market (Anwar, 2014). In 2007, in Portland thousands of children used toy trucks, helicopters and soldiers, sold under the brand name of Elite Operations. It was coated with a thick layer of glossy paint. The problem was found that the paint was loaded with 5000 ppm of lead, and this thick layer does not have a safe level of lead (Charles, 2008). The 100 toys were examined from leading, Chinese originals purchased online from JD: Taobao (TB) and Tmall (TM), which were sold in huge quantities. The games sold by JD and TM, which were considered organized vendors, showed Lead concentrations as 25 mg/kg and 32 mg/kg, respectively, The results were within determinants, while toys sold by unregulated vendors on the TB platform were 219 mg/kg. Approximately 12% of TB-purchased toys have a lead concentration higher than the determinants, while 36% exceeded the US regulatory standard equivalent and EU standard (Shen Z, 2018).

Iraq is one of the countries whose markets have been invaded by such Chinese products, in spite of the numerous reports of world that warned from the presence of heavy metals. In addition, Iraq has for many years been preoccupied with the security situation and internal battles without paying attention to children’s health. Therefore, this study was conducted to evaluate the heavy metals in the plastic toys, which include the products of the sellers in the popular platforms and malls, exploring the different factors that may be related to lead content in toys such as color, and children age.

2. Experiment

2.1. Sampling
Thirty-two toys were purchased from two different locations in Iraqi markets. The 16 toys purchased from Baghdad mall, and 16 toys from products of vendors in popular platforms in Baghdad. Selected according to (1) toy colors, black, red, and yellow, (note: previously studied show these colors contain high concentration of heavy metal) (Kumar, 2007), (2) cost (low cost predicted to contain high concentration of heavy metals), (3) the selected toys should be intended for three age groups, 3-12 months, 3-6 years and finally 1-3 years. All plastic samples are cut into small parts using mortar and pestle.

2.2. Chemical analyses
The 5.00 g of each sample is weighed from the prepared plastic toys cuts in the beaker. Add 5 mL of 69.7% concentrated nitric acid (HNO₃) to the plastic toys in the beakers and then heat on hot plate for 1 minute. Add 5 mL of 97% concentrated sulfuric acid (H₂SO₄) to the beakers and heat until brown smoke stops. Add 3 mL of 70% concentrated perchlorate (HClO₄) to the beakers and heat for 1 minute after the mixture become clear. Cooled and filtered through filter paper Whatman No.1. The leachate is placed in a 100 ml volumetric flask and the di-ionic water is added to the label. The blank was Prepared in the same manner (Livingstone, 2014).

The Standards were prepared with serial dilution technique within the range of 1–30 ppm for lead, nickel and cadmium. Each stock standard had a concentration of 1,000 mg/L supplied in 0.1 N HNO₃. As a way of ascertaining the reliability of the results, separately, recovery analysis was performed for each of the metal (Livingstone, 2014).

The samples were Analysis by Inductively Coupled Plasma–Atomic Emission Spectrophotometer (ICP-AES) in science and technology ministry.

2.3. Statistical analysis
Statistical analyzes were studied through the SPSS program Virgin 22 to analyze toys samples to illustrate the results and discuss parameters (e.g., geometric mean, standard errors, calculation of the significance of fitting).

The correlation matrix was also used, to illustrate the relationships between the variables such as concentration of lead - nickel and cadmium - colors, prices and age. In addition, to find the extent of correlation between them.

3. Result and Discussion
The results of 32 samples of plastic toys show in figure (1) the lead concentration in toys ranged from 8.0625 - 12.1875 mg / kg, while the nickel concentrations ranged between 7.125- 12.8125 mg / kg, cadmium concentrations ranged from 2.96875 - 4.0625 mg/kg. Because there is no Iraqi standard for metal concentrations in the paint of toys, we have adopted the standards of element migration of toy materials (ISO-8124-3), which defines concentration limits as 90 mg / kg for lead, 25 mg / kg for nickel and 75 mg / kg for cadmium and found all examined samples to have a lower concentration than the specifications, all the results far below the US EPA limit of 600 mg/kg for lead in painted toys. Livingstone and others (2014). The highest value of lead concentration appeared in the refrigerator toy, but the lowest values were found in the Lego toy. For nickel, the highest value was found in the refrigerator, and the lowest value emerged in Lego toy. For the cadmium concentration highest value was found in refrigerator, but the lowest value was in Weapon. All the results were lower than these results in the findings obtained by Abhay and Pranshant (2007) who analyzed plastic toys samples manufactured in India. From this study it was found that cadmium exists in a few concentrations and this means that it entered the manufacture unintentionally. For lead and nickel, it is possible to enter in the human body while children play with these toys and put them in the mouth. The presence of lead concentration indicates a risk of lead to children. Scientists and doctors agree that there is no safe concentration of lead in the blood. (Ab Latif Wani, 2015).

![Figure 1: concentration of Pb, Ni and Cd in toy](image_url)

The results showing the highest concentration for lead, nickel and cadmium are shown in figure (2).
The effect of toys price on the concentration of heavy metals are shown in figure (3). The results show that the concentration of lead in cheap toys is more than that in the expensive toys, which the difference is small. As well as in Nickel. However, the difference between cadmium concentrations in cheap toys and expensive toys is negligible.

The results show that the concentration of cadmium is small, but have relation with age of children, there was little differences between the children ages is negligible. However, the increase in concentration of cadmium increases with age. This is contrary to previous studies as (Oyeyiola, 2017), while the concentration of lead with the child's age is similar to cadmium. (3-6 years) contains the most concentrated followed by age (1-3 years), and then (3-12 months), and this also, applies with nickel, probably due to the toys that were made mostly black, such as gun, pistol and Whitman toy and others where dark colors contain the heavy metals of bright colors, These colors are undesirable in children under 1 year old. These results shown in Figures (4-5-6).
Color toys affect heavy metals: for lead, and Cadmium the highest concentrations are found in black, red, and yellow toys, progressively. While the highest concentrations of nickel appeared in black, yellow, and red progressively, because dark colors require more heavy metals than the rest of the colors, as shown in figures (7-8-9). These figures show that the concentration of lead, nickel and cadmium tends either to the center (normal distribution) or downward. This means that most readings are few and less
than the determinants and indicates the less pollution. The result of geometric mean, standard errors, Minimum, Maximum, and Variance during in SPSS program are shown in table (1).

| Table 1 Descriptive Statistics |
|-------------------------------|
| Pb   | Ni   | Cd  |
| Mean | 9.63 | 8.71 | 3.51 |
| N    | 32   | 32   | 32   |
| Std. Deviation | 1.080 | 1.248 | .269 |
| Median | 9.36 | 8.52 | 3.53 |
| Std. Error of Mean | .191 | .221 | .047 |
| Minimum | 8 | 7 | 3 |
| Maximum | 12 | 13 | 4 |
| Variance | 1.167 | 1.558 | .072 |
| Geometric Mean | 9.57 | 8.63 | 3.50 |

During the SPSS program, correlation matrix found the strong relationship between the concentration of lead, nickel and cadmium in addition to age, color and price. The strong relationships showing during significant (2-tailed) less than 0.05. from the results shown the strong correlation between Lead and other parameter, nickel and cadmium in addition to age, color except the price that significant (2-tailed) is weak 0.152, and show the strong correlation between the same variables with nickel except color that
significant (2-tailed) is 0.119 very weak. For cadmium, the correlation is found strong with all the variables. Due to all significant (2-tailed) is less than 0.05; these results are shown in table (2).

Table 2 correlation matrix

|       | Pb     | Ni     | Cd    | Age   | Color   | Price  |
|-------|--------|--------|-------|-------|---------|--------|
| Pb    | 1      | .795** | .882**| .787**| -.582** | -.259  |
|       | Sig. (2-tailed) |        |       |       |         |        |
| Ni    | .795** | 1      | .733**| .540**| -.281   | -.478**|
|       | Sig. (2-tailed) |        |       |       |         |        |
| Cd    | .882** | .733** | 1     | .759**| -.495** | -.362  |
|       | Sig. (2-tailed) |        |       |       |         |        |
| Age   | .787** | .540** | .759**| 1     | -.276   | .000   |
|       | Sig. (2-tailed) |        |       |       |         |        |
| Color | -.582**| -.281  | -.495**| .276  | 1       | .000   |
|       | Sig. (2-tailed) |        |       |       |         |        |
| Price | -.259  | -.478**| -.362 | .000  | .000    | 1      |
|       | Sig. (2-tailed) |        |       |       |         |        |

4. Conclusions
The concentrations of the heavy metals in all the toys were found in varying amount and the concentration of the lead is higher than nickel and the lowest amount in cadmium. The color effect on heavy metals shows the highest concentration in black then red and yellow, with the exception of nickel after black and then yellow and red, through the SPSS program, there is a significant relationship between lead, nickel, cadmium, age, color and price, except lead relationship is weak between price and nickel with color. According to the specifications of the US Environmental Protection Agency (ISO-8124-3), all readings are less than these determinants. However, the ability of heavy metals to accumulate in objects, children playing and putting the toys in the mouth, then transmission to the blood and damage to health, it is recommended for establishing specifications for the heavy metals in the paint of toys consistent with the Iraqi atmosphere, and then strict compliance thereof besides, tightening control of products entering the country.

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