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Original article

Lead, Cadmium, Arsenic and Nickel Content of Toy Samples Marketed in Turkey

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Metals including lead (Pb), cadmium (Cd), arsenic (As), and nickel (Ni) have been used for different purposes in industry. These metals can be found in the colourful components of toys such as clothes. Due to the fact that these metals cause different health problems, the usage of them in industry is still continuing to be regulated strictly. The aim of this study was to investigate the leaching of the above mentioned metals from dresses of toy samples marketed in Turkey. A total number of nine toys manufactured by six different countries were purchased and analysed by atomic absorption spectrophotometer for Pb, Cd, Ni and As leached from dresses of samples.The results were as follows: Pb levels were ranged from 0.03 to 1.78, Cd was from 0.37 to 21.11, Ni was from 0.37 to 21.11 mg/kg and As was under the detection limit. According to the measurements, Pb levels of all toy samples were below the levels stated in Turkish Standards Institute (TSE) but one sample's result was high. Cd and As levels were observed to be far below the threshold limis stated at TSE standard. There is no limit value for Ni in that standard. In spite of international regulations, some of toy samples can include significant amount of metals. These experimental evidences suggest that surveillance on toys for their metal levels should be done regularly for children's safety.

Key words: Lead, Cadmium, Arsenic, Nickel, Toy, Atomic absorption spectrometry.

Türkiye'de Satılan Oyuncak Numunelerinin Kurşun, Kadmiyum, Arsenik ve Nikel İçeriği

Kurşun (Pb), kadmiyum (Cd), arsenik (As) ve nikel (Ni) gibi ağır metaller farklı amaçlarda sanayide kullanılmaktadır. Bu metaller oyuncaklarda elbise malzemesi gibi özellikle renkli bileşenlerde bulunabilmektedir. Bu metallerin farklı sağlık sorunlarına neden olduğu gerçeği nedeniyle sanayi sektöründe kullanımları çok sıkı düzenlemeler ile devam etmektedir. Bu çalışmada Türkiye'de pazarlanan oyuncak örneklerinin elbiselerinde yukarıda belirtilen metallerin düzeyinin ölçülmesi amaçlanmıştır. Altı farklı ülke tarafından üretilen dokuz oyuncak bebeğin elbise kısmında Pb, Cd, Ni ve As düzeyleri atomik absorpsiyon spektrometresi ile incelenmiştir. Pb düzeyi 0.03 - 1.78 mg/kg, Cd 0.37 - 21.11 mg/kg, Ni 0.37 - 21.11 mg/kg ve As düzeyi ölçülebilir limitin altında tespit edilmiştir. Ölçümlere göre, sadece bir oyuncak örneğinin Pb düzeyi Türk Standartları Enstitüsü (TSE) tarafından belirtilen düzeyin üzerinde bulunmuştur. Cd ve As için değerler, TSE sınır düzeylerinin altında bulunmuştur. Ni için TSE tarafından hiçbir sınır değer belirtilmemiştir. Uluslararası düzenlemelere rağmen, bazı oyuncak örnekleri önemli miktarda ağır metal içerebilmektedir. Bu çalışma sonucunda çocukların güvenliği için oyuncakların metal seviyelerinin düzenli olarak izlenmesi gerektiği kanısına varılmıştır.

Anahtar kelimeler: Kurşun, Kadmiyum, Arsenik, Nikel, Oyuncak, Atomik absorpsiyon spektrometri.

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INTRODUCTION

Heavy metal poisoning has become an increasingly major health problem, especially after the industrial revolution. Heavy metals are found in water, food, air, household cleaners, cookware and other daily tools. Toys are an integral part of a child's developmental process. Children play with toys and learn about the world. But the chemical exposure of children from toys is an emerging concern. Heavy metal contamination of children's toys raises serious concern with the known toxic effects of them. Metals in toy materials and paints are loosely bound to the surface and can be easily leached. Typical behaviour of children such as chewing, licking and swallowing is a common source of heavy metal exposure from toys (1,2). Heavy metals such as lead (Pb), cadmium (Cd), arsenic (As), and nickel (Ni), pose a number of hazards to humans. These metals are also carcinogens and mutagens.

Different regulating agencies provide elemental content limits for a variety of toy sample types. The European Standard for safety of toys, EN 71, Part 3 contains one section entitled "Migration of certain elements". In this section it defines the limits of Pb, Cd and As migration from toy materials 90, 75 and 25mg/kg of toys respectively (3). These values are the same as Turkish Standards Institution (TSE) Standard (TS 5219 EN 71 3/April 1997) (4).

As a heavy metal, lead is widely used and is ubiquitous in the human environment as a result of industrialization. The widespread environmental contamination, the propensity to cause a wide spectrum of toxic effects and the number of individuals affected worldwide makes it a public health problem of global magnitude.Pbcan induce a wide range of adverse effects in humans depending on the dose and duration of exposure (2,5,6). In toddlers, anorexia is the earliest symptom of lead poisoning, followed by vomiting and irritability. Hyperkinetic behaviour, distractibility, impulsiveness, and anemia may be seen in chronic lead exposures. Signs and symptoms of chronic exposure in adults may include chronic renal failure, hypertension, teratogenesis, and impotence (7). In comparison with adult, children are more vulnerable to lead at increased risk for exposure and adverse health effects than adults due to their behavioural and physical charac teristics (5, 8). Pb has been linked to drops in IQ points, behavioural problems, and attention deficit hyperactivity disorder (1). Also the association of Pb exposure with increased human cancer risk was strengthened by recent studies, and inorganic Pb compounds were recently reclassified as probably carcinogenic to humans by the International Agency for Research on Cancer (IARC) (Group 2A) (9). The World Health Organization's (WHO) "safe" limit for Pb in blood, originally set in 1995, is 10µg/dL.

Cd is also a potential environmental pollutant. It is classified as a toxic element without any beneficial role in human physiology. Cd in the environment may enter the body through inhalation or ingestion (10, 11). Besides thetoxic effects of Cd on the lungs, kidneys, and bones, Cd is associated with occurrences of Itai-Itai, a disease under which patients show a wide range of symptoms such as low grade of bone mineralization, and high rate of fractures, increased rate of osteoporosis, and intense bone associated pain (10,12). Also IARC classified Cd as human carcinogen (Group1) (8,9,10,13).

Ni is a trace element, which is essential for many biological species, but is also a toxic metal whose actions that have not yet been fully explored. Human exposure to Ni occurs primarily via inhalation and ingestion. Exposure via inhalation has long been known to cause acute respiratory symptoms, ranging from mild irritation and inflammation of respiratory system to bronchitis, pulmonary fibrosis, asthma and pulmonary edema. Additionally, nickel exposure may cause cardiovascular and kidney diseases (14,15). Also several studies have demonstrated that Ni is the most widespread contact allergen in the general population and is most often identified as the leading allergen in children (16,17). Allergic contact dermatitis related to Ni accounts for up to 14.9% of positive patch tests in asymptomatic children and is generally more frequent in females (18,19). However, carcinogenic activity of Ni represents the most serious concerns. All Ni

compounds were recognized as human carcinogens (Group 1) and metallic nickel is classified as possibly carcinogenic to humans (Group 2B) according to IARC evaluation (9, 15).

As toxicity is a global health problem affecting millions of people. As exerts its toxicity by inactivating up to 200 enzymes, especially those involved in cellular energy pathways and DNA synthesis and repair. Chronic Asexposure may cause multisystem disease such as cardiovascular, nervous, hepatic, haematological, endocrine and renal. One of the hallmarks of chronic toxicity in humans from oral exposure to As are skin lesions, which are characterized by hyperpigmentation, hyperkeratosis, and hypopigmentation. As is also classified by IARC as a carcinogen in human (Group 1) (9, 20-22).

Although some epidemiological studies have been carried out on the health impacts of lead on children and its source in environment in Turkey (23-25), toys have not been investigated as one of the possible sources of lead, cadmium and other heavy metals. The aim of this study was to determine Pb, Cd, As and Ni leaching from cloth parts of baby toys imported to Turkey from different eastern countries using atomic absorption spectrometry.

EXPERIMENTAL

Chemicals

All chemicals and metal stock standard solutions were obtained from Sigma-Aldrich (St. Louis, MO, USA) and Merck (Darmstad, Germany).

Sample collection

A total number of 9 different toy samples manufactured by different countries were purchased from the markets in Turkey. These samples belong to six different producers.

Sample preparation

Sample preparation was carried out according to the 'TS 5219 EN 71 3/April 1997' standard (4). Briefly, dresses (textile part) of toys in different colours were cut as 100 mg from each dress material. Scissors are cleaned with ethanol after each contact with material. Each material sample from the same toy is taken into different falcon tubes and filled with 10 mL of 0.07 M HCl for extraction.

Each falcon tube was shaken for 30 seconds with 5 minutes interval while storing in water bath at 37^0C ± 2 for 1 hour. Then the 9 sample is stored in water bath additional 1 hour without shaking. Then each sample was taken from water bath. Liquid parts were separated from dress particles and transferred to another falcon tube. The HCl concentration of prepared solutions was adjusted to 1 M HCl for storage. Afterwards, to protect the samples from light, falcon tubes were coated with aluminium folio and placed into the fridge.

Measurement of the metals

Determinations of Pb, Cd, Ni and As in samples were done by graphite furnace atomic absorption spectrometry with Zeeman background correction (Analytic Jena, Zeenit 700). The calibration curve was plotted with standard solutions of Pb (10-40 µg/L), Cd (0.3-3 µg/L), Ni (2-20 µg/L) and As (3-30 µg/L). All measurements were done as triplicate and mean of these three values were used. The manufacturer's application notes were used for metal measurements checking validation parameters. Graphite furnace parameters were as follows (Table 1).

Table 1. Graphite furnace parameters.

(ºC)	Pb	Cd	Ni	As
Drying	90	90	90	90
Pyrolysis	900	800	1100	1080
Atomization	1400	1300	2350	2400

RESULTS

The result of the concentration of heavy metals in the various toy samples and the color of tested dress samples analysed is given in Table 2. Also bar graphs of the same data for each element are presented in Figure 1.

DISCUSSION and CONCLUSION

This study investigated the presence of some heavy metals in children toys imported into Turkey. Pb, Cd and Ni were found in all the tested toy samples invarying concentrations.

It was observed that Pb was present in all the analysed toy samples with a mean concentration of 17.84 mg/kg (ranging from 0.5 to 153 mg/kg). This mean Pb level is very high comparing with Cd, Ni and As. Regarding to the measurements, sample 1, 2, 3, 4, 5, 6, 7, 9 were containing 0.63, 0.85, 0.57 2.25, 0.64, 062, 0.53, 1.48 mg/kg Pb, respectively. These results are far below the threshold limit which is 90 mg/kg (4). On the other hand sample 8 showed high lead concentration (153 mg/kg) even exceeding the TSE limit of 90 mg/kg); this poses a threat to children exposed to such toys.

The Cd level in the toy-samples was observed to be far below the threshold limit of 75 mg/kg stated at TSE standard, with mean concentration of 0.24 mg/kg (ranged between 0.03 and 1.78 mg/kg). However it is widely accepted that no level of Pb and Cd in the blood should be considered safe for children and hence every effort should be made to ensure that their environment remains free from any such toxic metals (2).

It was observed that Ni was present in all the toy samples analysed in this study with a mean concentration of 4.33 mg/kg (varying from 0.4 to 21.11 mg/kg of samples).The threshold limit concentration for Ni was not stated but several studies have demonstrated that adult patients with normal skin, previously sensitized to Ni, may develop contact dermatitis at concentrations of 5–10 ppm. It is recommended that consumer products should not contain more than 5 ppm of this metal. However to minimize the risk for very sensitive individuals, it is recommended that the ultimate target should be not more than 1 ppm in consumer products (26,27). When we discussed about Ni release from toy samples Ni concentration in leaching medium can be a risk factor for dermatitis according to their Ni content. According to the Ni concentration in leaching medium for analysed samples, there can be a risk factor for contact dermatitis related with their Ni content.

As amount was at very low levels in some of tested samples (sample 1, 2, 4, 6, 7 and 8) and in some samples (sample 3, 5 and 9) levels were below the detection limit of 1.75 ppb.

The thresholds limit concentration for As is 25 mg/kg. The As levels except in samples 3, 5, and 9 (< LD) were observed to be far below

Table 2. Concentration of Pb, Cd, As and Ni in the dresses of toy samples analysed.

Toy Samples	Color of samples	**Pb**(mg/kg)	**Cd** (mg/kg)	**As** (mg/kg)	**Ni** (mg/kg)
Sample 1	Pink and yellow[b]	0.63±0.063	0.03±0.002	0.18±0.016	1.60±0.096
Sample 2	Blue and pink	0.85±0.042	0.04±0.002	0.16±0.012	8.30±0.415
Sample 3	Pink	0.57±0.066	0.04±0.003	< LD	1.82±0.167
Sample 4	Pink	2.25±0.068	0.14±0.003	0.25±0.013	1.67±0.117
Sample 5	Purple	0.64±0.045	0.04±0.004	< LD	0.40±0.032
Sample 6	Pink	0.62±0.044	0.03±0.002	0.11±0.009	0.86±0.051
Sample 7	Red	0.50±0.041	0.03±0.003	0.21±0.013	0.37±0.029
Sample 8	Blue	153±4.592	1.78±0.053	0.20±0.015	21.11±0.422
Sample 9	Yellow	1.48±0.092	0.04±0.003	< LD	2.82±0.192
Limit value[a]		90	75	25	-----
LD (ng/mL)		1.09	0.1	1.75	1.45
LQ (ng/mL)		3.3	0.3	5.3	4.4

Results were expressed as the mean of triplicates ± standard deviation (SD), [a]Limit values stated in TSE 5219 EN 71 standard for toy samples (mg/kg). LD: Limit of detection, LQ: Limit of quantification,[b]Colors are for illustrative purposes only.

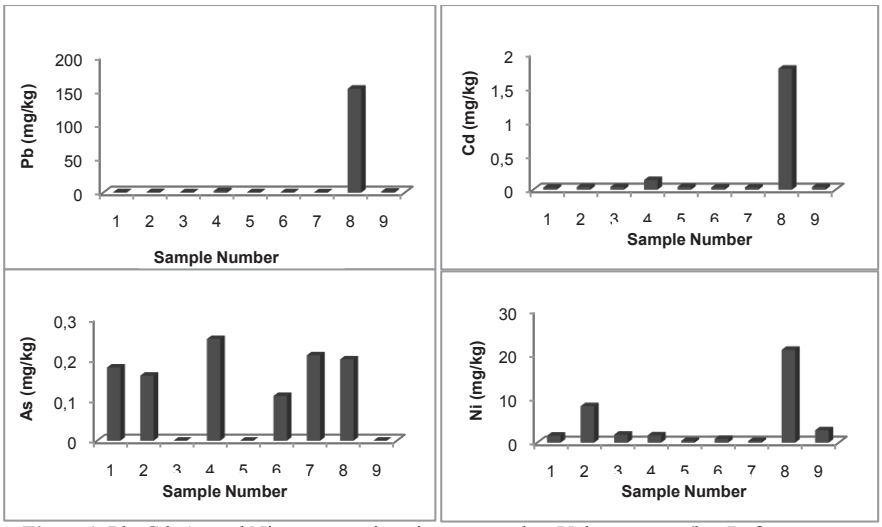

Figure1. Pb, Cd, As and Ni concentrations in toy samples. Values are mg/kg. Reference values stated in TSE 5219 EN 71 standard for toy samples are as follows: Pb: 90 mg/kg, Cd: 25 mg/kg, As: 25 mg/kg. There is no limit value for Ni in that standard.

the threshold limit of 25 mg/kg with a mean concentration of 0.18 mg/kg (0.11-0.25 mg/kg).

Reports by the contact dermatitis group of North America have consistently ranked Ni as the number one contact allergen on patch testing (28). Although there is no limit value for Ni in TSE, it has been recommended that consumer products should not contain more than 5 µg/g of Ni and preferably this level should be below 1 µg/g, in order to minimize the risk of allergic reactions (29,30). In our study, 6 of 9 samples exceeded the preferable limit of 1 µg/g and 2 of them were above the level of 5 µg/g.

As a conclusion, despite the regulations and restrictions children's toys imported into Turkey from different countries may still contain higher amount of toxic heavy metals than allowed limit. Toy samples with high levels of toxic heavy metals may pose hazards to children's health and may create environmental health hazards. In the absence of any leaching studies it is difficult to ascertain the levels of exposure that unbranded toys available in Turkey can cause hazards to children. As a result continuing research is required to increase understanding on potential heavy metal exposures and gather knowledge to minimize risks to children to any kind of heavy metals. Periodic market surveillance can be useful to maintain children's safety.

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