



Determination of Total Cadmium Content in Children's Arts Materials and Their Migration Test

AL-Shaibi Kawthar^{1*}, Massouh Laila², Zamrik Mohammad Amer³

1. Master degree in Toxicology, Faculty of Pharmacy, Damascus University, Damascus, Mezza Street, Syria.

2. Professor at the Department of Pharmacology and Toxicology, Faculty of Pharmacy, Damascus University, Damascus, Mezza Street, Syria.

3. Assistant professor at the Department of Pharmacology and Toxicology, Faculty of Pharmacy, Damascus University, Damascus, Mezza Street, Syria.

*Corresponding author's E-mail: kawtoxsh@yahoo.com

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ABSTRACT

Cadmium is a toxic metal, specially for children. It can be used in pigments of in arts materials for children to impart bright and glaze colors to them in order to attract children. The aim of the present article is the calculation of the total content of cadmium in children's arts materials and compared with the soluble migrated cadmium. A total number of 66 samples manufactured from different countries were purchased. The total cadmium content extraction by (EPA SW-846 3050 method) and the soluble migrated cadmium extraction by European method (EN 71- 3), then analyzed using atomic absorption spectrophotometer and inductively coupled plasma mass spectrometry to determine cadmium concentration. The results obtained show that cadmium was found in all samples, and ranged from (0.07-3.95 ppm) for total cadmium content. The soluble migrated cadmium ranged from (0.38 – 0.7 ppm), one sample did not reach detectable soluble level and (0.045-0.92 ppm) by atomic absorption spectrophotometer and inductively coupled plasma mass spectrometry respectively. The present study reveals that no clear correlation between the total amount of cadmium in the sample, and the soluble migrated cadmium. Some of the samples show high concentration (above Syrian limit) of cadmium; this poses a threat to children exposed to such products.

Keywords: Cadmium, children's arts materials, migration test, atomic absorption spectrophotometer, inductively coupled plasma mass spectrometry.

INTRODUCTION

Children begin to use arts materials at early ages in their homes, schools, child care facilities, churches, and other community gathering places. Arts materials include such things as crayons, chalks, pencils, pens, inks, paints, glazes, glues, modeling materials, adhesives, papers and solvents.¹ The greatest risk of dispersal obviously exists in those materials that are chemical products rather than other toys.²

Cadmium is a toxic metal and its the prime use in arts materials for children is in the manufacture of brilliant red, orange and yellow pigments that are used in them.³

Cadmium exposure can occur through ingestion. For instance, children are especially vulnerable to ingesting chemicals from art materials as they regularly put their hands into their mouths many times everyday⁴, they may taste art materials or swallow a product by mistake⁵ and by ingestion of scraped off materials are intended to be placed in the mouth, such as pencil.⁶ In Addition, children may expose to cadmium by Inhalation the dusts from mixing dry paints and clays.⁷ Both acute and chronic exposure are of potential concern.¹

Acute toxicity from ingestion of high levels of cadmium can result in abdominal pain, nausea, vomiting and death.⁸ Acute inhalation exposure to cadmium causes pulmonary inflammation and oedema.^{9,10} Chronic oral and inhalation exposure to cadmium leads to renal failure, characterized by proteinuria due to renal tubular dysfunction.^{11,12} The accumulation of cadmium in the

kidney affects renal vitamin D metabolism, which subsequently disturbs calcium balance that may lead to osteomalacia and osteoporosis.¹³

This, as well as the increased excretion of calcium may result in bone disease. The International Agency for Research on Cancer (IARC) has classified cadmium and cadmium compounds as *carcinogenic to humans* (Group 1), meaning that there is sufficient evidence for their carcinogenicity in humans.¹⁴ It can delay brain development in young children, leading to learning disabilities.¹⁵ And other health effects that can be caused by cadmium are reproductive disorders and possibly even infertility,¹⁶ damage to the central nervous system, damage to the immune system and psychological disorders.¹⁷

The current toy standard in Syria

The Syrian standard (S.N.S:2465/2001)¹⁸ has been adopted from European Standard Safety of Toys-Part 3: Migration of certain elements (EN 71-3:1994)¹⁹ which covers any toy material, clay, and finger paint, in addition to paints and coatings, with specified test methods. The migration limit of cadmium was summarized in (Table1). The Syrian standard (S.N.S:2627/2002)²⁰ has been adopted from Australia standard (1647/1982) which limits the cadmium content in modelling clay shall not be exceeded 0.05ppm.



Table 1: The Syrian standard (S.N.S:2465/2001)

Element	Sb	As	Ba	Cd	Cr	Pb	Hg	se
Any toy material, except modeling clay and finger paint	60	25	1000	75	60	90	60	500
modeling clay and finger paint	60	25	250	50	25	90	25	500

The primary goal of this study was to determine total cadmium content in some Syrian-made children's arts materials and the imported ones. Then compare total cadmium content with soluble migrated cadmium.

MATERIALS AND METHODS

Apparatus

- Atomic absorption spectrophotometer (Varian spectraAA.200, Australia).
- Inductively coupled plasma mass spectrometry (Agilent 7500 ce, USA).
- Muffle furnace (Heraeus GMBH. Hanau, Germany).
- Hot plate (Memmert, Germany).
- Dry oven (J.P. Selecta,s.a, Spain).
- pH Meter BT-600 (Boeco, Germany).
- Centrifuge (Heraeus, Germany).
- Mixture (Thermolyne, USA).

Materials

All chemical used were of analytical grade.

- Nitric acid 65% (Merck, Germany).
- Hydrogen Peroxide 33% (Merck, Germany).
- Hydrochloric acid 37% (Merck, Germany).
- Distilled water.
- Stock standard solution of cadmium 1000ppm (Merck, Germany).

Samples collection

Total of 66 samples were purchased randomly from Damascus and Aleppo cities in Syria.

The samples included 4 chalks, 6 face paints, 4 finger paints, 13 color pencils coating, 13 color pencils lead, 2 color papers, 7 modelling clays, 6 wax crayons, 11 watercolors. With different color yellow, red, blue, green, orange, mauve, pink, white, black.

Samples preparation

Total cadmium content

The methodology included subjecting samples first to ashing and then digesting in accordance with EPA SW-846 3050²¹ (digestion with nitric acid and hydrogen peroxide).¹⁷ 10g of the sample was broken into several pieces in a

large silica crucible and charred on a hot plate till the fume ceased to exist, followed by complete ashing in muffle furnace at 480°C for 4 hours. The crucible was then taken out of the furnace and kept in dry oven for cooling. After cooling, the samples were powdered and homogenized in the silica crucible. Then the sample was taken in separate silica crucible for acid digestion. Nitric acid and hydrogen peroxide were used for digestion in an open vessel. After complete digestion the samples were transferred to 100 ml Tarson bottles and the volumes were made 100 ml. Blank samples were also prepared similarly.¹⁷

Standards were prepared with serial dilution technique within the range (0.5–2 ppm) for cadmium. The samples were quantitatively analysed using AAS with flame at wavelength 228.8 nm. The instrument was calibrated with standards prepared from stock solution. After every ten samples analysed using FAAS, the first sample was repeated for quality check. Only when the results were within 10% of earlier readings did the analysis proceed further.

Soluble migrated cadmium

The principle of the procedure in EN71-3:1994 is the extraction of soluble elements from toy material under the conditions simulating the material remaining in contact with stomach acid for a period of time after swallowing.¹⁹ 200 mg of the sample with particle size \leq 0.5 mm were suspended/dissolved in 10 ml of 0.07 M aqueous HCl and pH was adjusted to \leq 1.5 using 2 M HCl. The mixture was shaken for 1 hr at 37 ± 2 °C and thereafter allowed to stand at same temperature for an hour. This was followed by centrifugation of the mixture for 2min at 600g. The extract was filtered through a 0.45 μ membrane filter and analyzed within 24 hours. Blank sample was also prepared similarly.²²

The final processed samples were quantitatively analysed using FAAS and ICP-MS. The ICP-MS using argon plasma at 8000 °C was used under following conditions:²² plasma flow 15.75 L/min, nebulizer flow 0.85 L/min, auxiliary flow 0.91 L/min, RF power 1030 watts, CEM voltage 4.9 kV, sample uptake 1 ml/min, m/z for cadmium 114. The instrument was calibrated with standards prepared from cadmium stock solution within the range (0.5–30 ppb).

RESULTS AND DISCUSSION

This study investigated the use of cadmium in children's arts materials found in Syria. Cd was found in all the tested samples in varying concentrations, ranged from (0.07-3, 95 ppm).

Sample type, origin, sample color and the result of the total cadmium content in the all samples were analysed are given in (Table 2).

Table 2: The total cadmium content (ppm)

Sample number	type sample	origin	Sample color	Cadmium con (ppm)
Dry, brittle, powder-like or pliable toy materials				
1	Chalk	Syria	yellow	0.26
2		Syria	blue	0.245
3		Syria	red light	0.195
4		Syria	green light	0.1925
5	Face paint	Korea	red	0.972
6		Korea	yellow	1.275
7		Korea	green	1.275
8		Korea	blue	1.275
9		Korea	black	0.55
10		Korea	white	0.86
11	Modeling clay	China	red	1.10
12		China	yellow	1.10
13		China	blue	0.07
14		China	green	0.11
15		China	orange	1.16
16		China	pink	1.16
17	Wax crayon	China	mauve	0.32
18		Syria	red	1.15
19		Syria	red deep	42.4
20		Syria	yellow	1.075
21		Syria	green	1.075
22		Syria	blue	1.175
23	Color paper	Syria	pink	1.35
24		Syria	mauve	1.65
25		Italy	red	0.96
26		Italy	orange	1.19
27		China	yellow	0.26
28		China	red	0.22
29	Color pencil lead	China	red deep	0.36
30		China	green	0.33
31		China	green light	0.24
32		China	blue	0.35
33		China	blue light	0.34
34		China	mauve	0.36
35		China	pink	0.17
36		China	black	0.33
37		China	white	0.19
38		Brazil	yellow	0.448
39		Brazil	red	0.408
Liquid and sticky toy materials				
40	Finger paint	Holland	green	0.82
41		Holland	red	0.70
42		Holland	yellow	1.02
43		Holland	blue	0.68
44	Water color	Syria	yellow	1.65
45		Syria	red	1.82
46		Syria	blue	1.85
47		Syria	mauve	1.775
48		Syria	green	1.55
49		China	red	3.15
50		China	yellow	1.37
51		China	green	1.175
52		China	blue	1.625
53		China	orange	1.25
54	China	mauve	3.95	

Scraped-off toy materials				
55	Color pencil coating	China	yellow	0.24
56		China	red	0.20
57		China	red deep	0.37
58		China	green	0.33
59		China	green light	0.24
60		China	blue	0.37
61		China	blue light	0.34
62		China	mauve	0.37
63		China	pink	0.63
64		China	black	0.34
65		China	white	0.66
66		Brazil	yellow	0.265
67		Brazil	red	0.270

The averages of total cadmium content in yellow, red, blue, green, mauve, pink, orange, black, white samples are 0.824, 0.848, 0.75, 0.66, 1.40, 0.827, 1.2, 0.40, 0.57 respectively.

The total content of cadmium increased in mauve, orange, red, pink, yellow, blue, green, white and black respectively. In fact cadmium pigments produce wide spectrum of colors includes yellow, orange, and red shades, and other colors (such as green, brown, beige) that may be based on yellow or red.¹² All cadmium pigments are based on cadmium sulfide, the addition of zinc produces greenish yellow pigment while mercury and selenium produce orange, red and deep red shades and addition of cobalt produce green.²³

The result of the soluble migrated cadmium and their total content of cadmium in the 10 samples analyzed are given in (Table 3).

We can notice in figure 1, there is no clear correlation between the total amount of cadmium in an arts material sample, and the soluble cadmium that migrate out of the sample in HCl. Both the physical design of a product and the chemical composition can affect the bioavailability of a specific chemical.¹ Ian A. Elder, study on children's jewelry was showed that soluble cadmium migration not only proportional to cadmium content. It found that a product composition factor such as element content had larger effect on cadmium migration than total cadmium content.²⁴

It was observed that majority 53% of the samples analyzed in this study were made from China, 9% from Korea, 6% from Holland, 6% from Brazil, 3% from Italy and 23% from Syria. This was attributed to the fact that China is the largest toy seller in the world; nearly 80% of the world's toys are made in China.²⁵

There is no enforceable standard for the total content of cadmium and other toxic metals in toys in Syria. The results of total cadmium content analysis in the arts materials tested (except modeling clay) were compared with the Syrian standard (S.N.S:2465/2001); no sample above the threshold limit of 50mg/kg were recognized, and the mean concentration was 1.45 mg/kg. This can be attributed to the fact that cadmium and several

cadmium-containing compounds have been reported to be carcinogenic and can induce many types of cancer. Cadmium is one of the six substances banned by the European Union's Restriction on Hazardous Substances

directive.²⁶ Cadmium pigments accounted for 20% to 30% of cadmium consumption between 1970 and 1990 but declined to 12% in 2000.²⁷

Table 3: Comparison of the soluble migrated cadmium and the total cadmium content (ppm)

Sample number	type Sample	Origin	Total cadmium content ¹	Soluble migrated cadmium ¹	Soluble migrated cadmium ²
1	Yellow modeling clay	China	1.10	0.52	0.455
2	modeling clay Red	China	1.10	0.45	0.9205
3	Yellow face paint	Korea	1.27	0.66	–
4	Red face paint	Korea	0.97	0.7	–
5	color paper Red	Italy	0.96	0.63	–
6	water color Green	Syria	1.55	0.56	–
7	water color Mauve	china	3.95	0.7	–
8	finger paint Red	Holland	0.70	0.38	0.0455
9	Finger paint Yellow	Holland	1.02	0.46	0.1435
10	Yellow pencil coating	china	0.24	ND	–

ND: not detectable. 1:by FAAS. 2: by ICP-MS.

Table 4: 2009/48/EC and 2012/7/EU migration limits of cadmium from toys

Cadmium (mg/kg)	In dry, brittle, powder-like or pliable toy material	In liquid or sticky toy material	In scraped off toy material
2009/48/EC	1.9	0.5	23
2012/7/EU	1.3	0.3	17

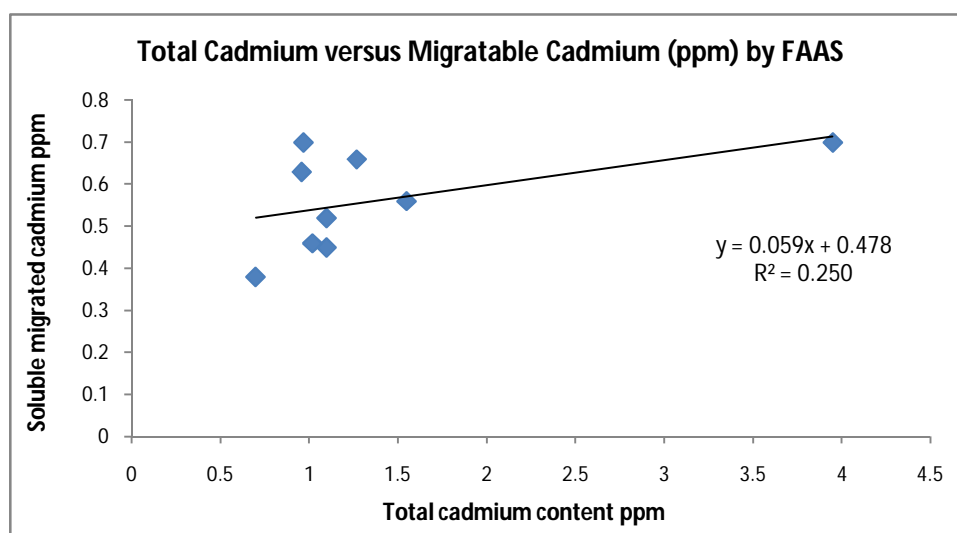


Figure 1: Total cadmium content in art materials versus soluble migrated cadmium measurements by FAAS.

For modeling clay, the average (0.717ppm) exceeded the Syrian limit (0.05ppm). Existing differences toy safety standards globally and increases in international and internet commerce. In addition, many of the current labeling rules and standards may predate the internet and may not be universally applied by internet based merchants have created new challenges. For example, in the mid-1990s crayons imported into the US labeled as

"non-toxic" appeared on the market, were discovered to contain high levels of lead, and were recalled.¹

It is now widely accepted that there's no safe level of cadmium for children to be exposed to.²⁸ In 2009, the European Toy Safety Directive 2009/48/EC sets new migration limits for accessible parts or components of toys.²⁹ The cadmium migration limits have been further reduced to 72% of the original values by directive 2012/7/EU; the limit was listed in (Table 4).³⁰

CONCLUSION

Cadmium was found in all tested children's arts materials. No clear correlation between the total amount of cadmium in a sample, and the soluble migrated cadmium. Some of the samples show concentration exceeding the Syrian limit of cadmium; this poses a threat to children exposed to such products.

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