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# Migration of Some Toxic Metals from Crayons and Water Colors

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Antimony (Sb), arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), mercury (Hg), lead (Pb) and selenium (Se) are among the many metals which have been shown to be toxic to human health and the environment (Berman 1980; Bertram et al. 1985; IPCS 1981, 1987, 1988, 1989a, 198973, 1990, 1992,). Various metallic pigments and colors in the form of salt or lakes are used in the production of toys. Children may thus be exposed to toxic metals when playing with toys, especially when they are licking or sucking the toys, or in the worst case when they swallow a toy or a piece of a toy. To protect children against toxic metals, the toys in European Union Markets must conform to the EEC Directive on safety of toys (Council Directive 1988). One of the restrictions according to the toy directive concerns the bioavailability of the above mentioned elements from the toy materials: paints, paint coatings, papers, textiles, materials used for writing and drawing, etc. The maximum limits for bioavailability per day from the accessible parts of a toy are set to 0.5 µg Sb, 0.1 µg As, 25.0 µg Ba, 0.6 µg Cd, 0.3 µg Cr, 0.7 µg Pb, 0.5 µg Hg and 5.0 µg Se (Council Directive 1988).

To achieve the maximum bioavailability limits of the above mentioned 8 elements, migration limits of these elements from toy materials have been set in European Standard EN 71-3 (CEN 1988). Thus, the migration of the 8 elements from toy materials, under the conditions defined in EN 71-3, should not exceed the values described in Table 1. In the present investigation we determined the migration of As, Ba, Cd, Cr, Hg, Pb, Sb and Se under the EN 71-3 defined conditions to evaluate whether the crayons, water colors and water-based paints (some of the most common toy materials for children up to age of 12 years) conform with the migration limits of these elements. Another aim of the study

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was to determine the specific metals that children may be exposed to during their play (use) with the above mentioned toy materials.

Table 1. Limits of element migration from accessible parts of toy material.

| Toy material | Migration limits (mg/kg) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Sb | As | Ba | Cd | Cr | Pb | Hg | Se |
| All materials except modelling clay and finger paints | 60 | 25 | 500 | 75 | 60 | 90 | 60 | 500 |
| Modelling clay and finger paints | 60 | 25 | 250 | 50 | 25 | 90 | 25 | 500 |

## MATERIALS AND METHODS

Danish manufacturers/importers of crayons and water colors provided samples for analysis. All in all 48 products from China, Taiwan, Japan, USA and EU countries were obtained for the analysis. Twenty three of the products were crayons, 23 were water colors and paints of various colors and 2 contained both crayons and water colors. Three products were comprised of neon colors: 2 paint boxes with water colors and a crayon product. For the analysis, 94 samples were selected such that all the products were represented and at least 10 samples of the most common colors (red, green, blue, yellow and white) were analyzed (Table 2).

Migration of metals from crayons and water colors was determined according to the methods described in EN 71-3 (CEN 1988). In brief, all glass and plasticware were specially cleaned as required for trace metal analyses and precautions were taken not to contaminate the analysis by any source which may leach the target elements. A crayon was scraped to thin flakes and 200 mg of the scraped material was degreased by soxhlet extraction with dichloromethan (pretreated with 0.15 M HCl) for 2 hr at 54°C. The degreased material was suspended in 10 mL of 0.07 M aqueous HCl and pH of the suspension was adjusted to $\leq 1.5$ using 2 M HCl. The mixture was shaken for 1 hr at 37.0 ± 0.2°C and thereafter allowed to stand at the same temperature for an hour. This was followed by the centrifugation of the mixture for 2 min at 600g. The extract (supernatant) was filtered through a 0.45µ membrane filter and analyzed within 24 hours for the 8 target elements by induc-

Table 2. Colors of the investigated crayons.

| Color | No. of samples | | |
|---|---|---|---|
| | Crayons | Water colors | Total |
| Red | 6 | 7 | 13 |
| Blue | 8 (1) | 8 | 16 |
| Yellow | 9 | 7 | 16 |
| Green | 7 | 7 (1) | 14 |
| White | 5 | 6 | 11 |
| Black | 3 | 2 | 5 |
| Brown | 3 | 2 | 5 |
| Violet | 3 | 1 | 4 |
| Pink | 2 | 2 (1) | 4 |
| Grey | 1 | - | 1 |
| Orange | 3 | 2 | 5 |

Numbers in parenthesis are samples with neon colors.

tively coupled plasma - mass spectrometry (ICP-MS) . A reagent blank, without sample, was prepared exactly as the sample. All the samples were run in duplicate.

A water color was crushed to fine particles and passed through a 0.5-mm sieve. Two hundred mg of the material with particle size 10.5 mm were suspended/dissolved in 10 ml of 0.07 M aqueous HCl and thereafter treated as for the crayons. A water-paint sample (200 mg) was suspended in 10 mL of 0.07 M aqueous HCl and treated as above.

A Perkin Elmer-SCIEX ICP-MS, ELAN 5000, was used for the analysis of the 8 target elements using argon plasma at 8000°C. Data collection and calculation of element concentration were performed employing ELAN software. One thousand ppm stock solutions (PE Pure Atomic Spectroscopic Standards) of Sb, As, Ba, Cd, Cr, Hg, Pb and Se from Perkin Elmer were used as metal standards. The ICP-MS was used under following conditions: 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 (employing Gilson 212 autosampler and Gilson 312 peristaltic pump). Positive ionization of elements was initiated in peak hop scanning mode and 3 replicate readings at peak

maxima were used for data collection. Elemental analysis was performed in the selective ion mode using m/z 75 for As, 114 for Cd, 121 for Sb, 138 for Ba, 202 for Hg and 208 for Pb; which are the major naturally occurring isotopes of these substances. Some interferences were observed in the determination of major isotopes of Cr (m/z 52) and Se (m/z 80). Therefore, content of Cr in the sample extracts was determined as $^{53}Cr$ (prevalence 10%) and Se content was determined as $^{82}Se$ (prevalence 9%).

## RESULTS AND DISCUSSION

The ICP-MS method used for the analysis of metals was suitable for the investigation of migration of elements, as the low concentrations of all of the 8 target elements could be determined in a single run; within 24 hr after the sample preparation. The detection limits of all of the 8 target elements analyzed in the present investigation were below 0.1 ppb. The calibration curves for the metal standards were linear ($r^2$ >0.999) in the investigated concentration range: 0.05-1.0 ppm for Sb, Cd, Cr and Hg, 0.02-0.4 ppm for As, 0.08-1.60 ppm for Pb and 0.5-80 ppm for Se. The calibration curve or Ba was found to be linear; however, only in the concentration range 0.40-3.0 ppm. The sample extracts, which showed concentrations of the target element(s) over the linear range, were appropriately diluted and reanalyzed. This was often the case with the analysis of barium. The relative standard deviation of the method of elemental analysis was l-11% for the target elements.

Migration of all target elements, except Cr and Se, occurred from both crayons and water colors. Chromium and Se migrated only from crayons but not from water colors. Among the investigated red, blue, green, yellow and white samples, 35-81% showed migration of As/Ba/Hg/Pb. However, only 0-37% of the samples with the same colors revealed migration of Sb/Cd/Cr/Se. Samples with white colors did not reveal any migration of Cd, Cr and Se. No migration of Se was found from red, blue, green or yellow samples. Statistical distribution of migration of elements from samples with other colors was not calculated because they represented very small sample numbers.

The migration of target elements from the investigated samples are described in Table 3. Cadmium (0.03-0.42 ppm) migrated from 10% of the investigated samples, Sb (0.17-0.49 ppm) from 17% samples and Cr (0.25-21.73 ppm) migrated from 19% of the samples. Barium migration (0.21-540.50 ppm) was revealed by 46% of the samples.

Table 3. Migration of elements from the investigated samples.

| Sample-color | No. of samples | Cr-migration n* | Cr-migration ppm | As-migration n* | As-migration ppm | Se-migration n* | Se-migration ppm | Cd-migration n* | Cd-migration ppm |
|---|---|---|---|---|---|---|---|---|---|
| Red | 13 | 2 | 0.25, 0.56 | 5 | 0.20-3.75 | 0 | - | 2 | 0.14, 0.36 |
| Blue | 16 | 6 | 2.08-5.32 | 12 | 0.03-1.13 | 0 | - | 2 | 0.33, 0.41 |
| Yellow | 16 | 2 | 1,05, 1.10 | 7 | 0.03-0.49 | 0 | - | 1 | 0.14 |
| Green | 14 | 4 | 1.59-5.37 | 10 | 0.01-0.32 | 0 | - | 1 | 0.42 |
| White | 11 | 0 | - | 6 | 0.11-0.56 | 0 | - | 0 | - |
| Diverse | 24 | 4 | 15.3-21.73 | 12 | 0.06-0.81 | 2 | 0.02-0.75 | 3 | 0.03-0.15 |
| **Total** | 94 | 18 | 0.25-21.73 | 52 | 0.01-3.75 | 4 | 0.02-0.75 | 9 | 0.03-0.42 |

| Sample-color | No. of samples | Sb-migration n* | Sb-migration ppm | Ba-migration n* | Ba-migration ppm | Hg-migration n* | Hg-migration ppm | Pb-migration n* | Pb-migration ppm |
|---|---|---|---|---|---|---|---|---|---|
| Red | 13 | 2 | 0.26, 0.43 | 6 | 2.95-211.48 | 9 | 0.24-5.98 | 7 | 0.23-24.27 |
| Blue | 16 | 2 | 0.35, 0.38 | 8 | 0.21-330.00 | 8 | 0.26-3.63 | 8 | 0.42-4.34 |
| Yellow | 16 | 3 | 0.24-0.49 | 6 | 1.59-413.65 | 10 | 0.20-4.79 | 8 | 0.05-3.51 |
| Green | 14 | 2 | 0.40, 0.48 | 5 | 2.14-399.12 | 7 | 0.22-5.68 | 6 | 0.45-8.21 |
| White | 11 | 2 | 0.22, 0.27 | 5 | 2.50-540.50 | 9 | 0.17-3.63 | 5 | 0.12-2.33 |
| Diverse | 24 | 5 | 0.17-0.32 | 5 | 9.97-392.40 | 14 | 0.24-5.99 | 11<br>1 | 0.03-3.84<br>436.84 |
| **Total** | 94 | 16 | 0.17-0.49 | 43 | 0.21-540.50 | 57 | 0.17-5.99 | 54 | 0.03-436.84 |

* number of samples which revealed migration of respective elements.

Migration of Ba from water colors (>100 ppm) was relatively higher than that from crayons (150 ppm) . Migration of As (0.01-3.75 ppm), Hg (0.17-5.99 ppm) and Pb (0.03-436.8) under experimental conditions was revealed by 55-60% of the investigated samples. One of the samples (a black crayon) revealed Pb migration to 437 ppm, almost 9 times the maximum allowed migration limit of this element. Excluding this sample, the migration of Pb from the investigated samples was 0.03-24.27 ppm. Only 4 samples (4%) revealed migration of Se (0.02-0.75 ppm) .

The maximum limits of bioavailability and migration limits of the 8 elements from toys were set with not enough knowledge of the content/migration of these elements from toy materials (CEN 1988). An average daily intake of 8 mg toy material by a child was considered when setting the maximum migration limits of the target elements from toy materials. It was, however, recognized that in some cases the daily intake of toy material(s) by a child may be higher. However, no consideration was given to the accumulative daily intake of elements from toy materials when setting the limits for the bioavailability or migration of elements. Crayons, water colors and water-paints (including finger paints) are the toy materials that are commonly used by the children up to age of 12 years. The results of the present study revealed that a child may be exposed to 4-8 of the target elements simultaneously during the use of (play with) crayons/water colors. Furthermore, a child may play with different toys (toy materials) during a day, and, thus, he/she may be exposed to several of the 8 regulated elements simultaneously. Thus, the accumulative bioavailability of the 8 elements to children may be rather high, eventhough each toy material may meet the regulations concerning migration limits/bioavailability limits of individual elements. Moreover, experiences with child behavior may suggest that they either simply lick a toy (material) or they may eat up to several grams of the toy material(s). Thus, intake of toy material by a child in special cases may increase by many folds of 8 mg. It may, therefore, be argued that a reexamination of the migration limits of the elements from toy materials is necessary. Data obtained in the present study may be an aid to the reevaluation of the migration limits. During reevaluation of migration limits, the migration limits of other toxic elements, for example Co and Ni (pigments of these elements may be used in the production of toys) should also be included. Furthermore, it might be useful if the migration limit for hexavalent chromium is differentiated from that of trivalent chromium,

because the toxic potentials of these two forms of chromium are much different (IPCS 1988).

The results of the present study also indicate that crayons and water colors may not be an insignificant source of pollution of the environment by toxic metals. Analysis of the total content of various toxic metals in crayons and water colors is required to estimate the load of toxic metals from these materials.

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