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INVESTIGATIVE REPORT

Measurement of Nickel, Cobalt and Chromium in Toy Make-up by Atomic Absorption Spectroscopy

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Cosmetics should not contain more than 5 ppm of nickel, chromium or cobalt and, in order to minimize the risk of sensitization in very sensitive subjects, the target amount should be as low as 1 ppm. However, there are no published reports on the presence of these metals in toy make-up. This study analysed 52 toy make-ups using atomic absorption spectroscopy. More than 5 ppm of nickel was present in 14/52 (26.9%) samples. Chromium exceeded 5 ppm in 28/52 (53.8%) samples, with values over 1000 ppm in 3 eye shadows. Cobalt was present in amounts over 5 ppm in 5/52 (9.6%) samples. Powdery toy make-up (eye shadows) had the highest levels of metals, and "creamy" toy make-up (lip gloss and lipsticks) the lowest. Toy make-ups are potentially sensitizing items, especially for atopic children, who have a damaged skin barrier that may favour penetration of allergens. ***Key words: toy make-up; atomic absorption spectroscopy; nickel; cobalt; chromium.***

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Nickel, chromium and cobalt are common contact allergens, which are present not only in metallic objects but also in tanned leather, tattoo pigments and cosmetics. Cosmetics represent an important source of sensitization, since they are used every day and are applied to the thinnest areas of facial skin, such as the peri-ocular areas and lips, where absorption is very high (1).

The presence of nickel, chromium and cobalt in cosmetics is forbidden by European Law 76/768/EEC (2), but their presence is permitted in very low quantities, defined as "impurities", if it is "technically necessary". However, there is no information about the amount of these metals that should be defined as an "impurity" and the methods to be used to quantify such traces.

The scientific literature proposes a value for nickel, chromium and cobalt lower than 5 ppm as "good manufacturing practice", while the "target" amount to minimize the risk of sensitization in particularly sensitive subjects should be as low as 1 ppm (3, 4).

Whilst such considerations are set out for cosmetic products, there is little information about toy make-up. These items, which are widely commercially available, are applied on the thin skin of children's faces and stay on for variable periods, often as long as real cosmetics. Toy cosmetics are usually sold in kits, boxes containing different toy make-up, such as eye shadows, lipsticks, lip glosses, etc. The kit is a toy and should fulfil the requirements of the toys directive, while each product in the kit is a cosmetic product and should meet the cosmetic directive (2, 5).

The aim of this study was to analyse different types of toy make-up, using atomic absorption spectroscopy, for the presence of nickel, chromium and cobalt and to quantify their concentrations.

MATERIALS AND METHODS

Materials

Seven toy make-up kits, numbered 1–7, were bought in different shops (e.g. toy shops, hypermarkets, tobacconists, newsagents (as gifts in children magazines) and bazaars). Each box included various cosmetics (e.g. eye shadows, lip gloss, lipsticks, nail polish, lip pencil, lip balm).

A total of 52 cosmetics were analysed: 29 eye shadows, 15 lip glosses, 5 lipsticks, one nail polish, one lip pencil and one lip balm. The samples were processed by acid digestion in a microwave oven. A 0.2–0.4 g weight of each cosmetic was taken and 6 ml concentrated nitric acid, 2 ml concentrated hydrofluoric acid and 2 ml 30% hydrogen peroxide were added. The samples underwent a specific microwave program using a ETHOS 900 microwave oven (Milestone, FKV, Sorisole, Italy) equipped with a six-position mono-bloc high pressure rotor.

After cooling, the samples were transferred to 50 ml volumetric flasks and diluted to the mark with MilliQ water (Millipore Corporation, Bedford, USA). When necessary, samples were filtered through N41 ash-less filters (Whatman International Ltd, Maidstone, UK).

Method of analysis

All measurements were carried out with a model analyst 800 atomic absorption spectrometer (Perkin-Elmer, Shelton, USA) equipped with a Zeeman background correction system and an electrothermal atomizer with a transversely heated graphite tube.

Atomic absorption spectroscopy was performed at a wavelength of 236.0 nm for nickel, 356.9 nm for chromium and 242.5 nm for cobalt. Matrix modifier was applied for chromium and cobalt ($Mg(NO_3)_2$). The volume of each analysed sample was 20 µl. Each sample was prepared twice, two different analyses were performed, and the mean value calculated.

The detection limits were defined as the analyte concentration corresponding to 3 times the standard deviation of 10 consecutive blank sample runs, using 200 mg of the solid sample in a final volume of 50 ml. This value was 0.1 μg/g for chromium and nickel, and 0.2 μg/g for cobalt.

The accuracy of the analysis was demonstrated to be between 95% and 105%, by the recovery data observed for spiked real samples (6, 7).

RESULTS

The quantities (mean values) of nickel, chromium and cobalt detected in each toy make-up are shown in Table I. The number of samples of each type of make-up, grouped by metal content, are shown in Table II. Values are grouped as 1–10 ppm, 10–100 ppm, 100–1000 ppm, and more than 1000 ppm.

For the 29 eye shadows (total number of analyses performed = 87), in 3 cases the presence of chromium was a lot higher than 1000 ppm (1580 ppm, 3620 ppm and 1579 ppm). In 38 out of 87 tests, nickel, chromium and cobalt were more than 10 ppm. In 39 analyses the quantity of metals was between 1 and 10 ppm.

For the 5 lipsticks, no values higher than 10 ppm were detected. Levels between 1 and 10 ppm of nickel and chromium were obtained in 5 and 2 samples, respectively.

For the 15 lip glosses, no values higher than 10 ppm were detected. In 3 samples chromium was in the range 1–10 ppm.

Table III shows the values of the three metals in the range 0–5 ppm. The results for the 29 eye shadows show that this amount of nickel, chromium and cobalt was present in 15, 3 and 24 samples, respectively.

All 15 lip glosses contained quantities of nickel and cobalt between 0 and 5 ppm. Only one had higher quantities of chromium. The quantity of chromium exceeded 5 ppm in 1 of the 5 lipsticks, while all the other metals were in the range 0–5 ppm.

None of the 29 eye shadows met the amount of 1 ppm or below for nickel and chromium, 10 contained an amount of cobalt no higher than 1 ppm. All 15 lip glosses were in this range for nickel and cobalt; 3 lip glosses contained more than 1 ppm of chromium. The 5 lipsticks contained over 1 ppm chromium, while the amount of cobalt was always lower.

Table I. *Quantities (mean values) of chromium, nickel and cobalt in toy make-ups*

Toy make-up type and colour	Nickel μg/g (ppm)	Chromium μg/g (ppm)	Cobalt μg/g
Box/kit 1			
Eye shadows			
lavender	262	203	12.0
lilac	320	290	12.5
Lipsticks/mallow	1.23	2.89	<0.2
Box/kit 2			
Eye shadows			
dark green	1.8	1580	0.99
light green	1.9	106	0.99
pale green	10.1	47.7	1.04
dark salmon	4.4	30.4	1.2
pale salmon	1.4	16.7	1.13
blue	2.5	61.8	0.61
sky blue	2.0	35.5	0.86
light violet	10.1	41.3	1.2
magenta	10.2	26.3	1.1
pink	11.2	23.3	1.3
grass green	6.9	32.3	1.5
yellow	9.5	37.2	0.84
Lipsticks/red	0.14	1.33	<0.2
Box/kit 3			
Eye shadows			
apricot	2.33	1.61	1.26
lavender	2.96	3.03	1.25
pink	2.65	2.72	1.45
grey	5.47	3620	5.46
yellow	2.52	19.3	1.14
Lipsticks/red	<0.1	1.1	<0.2
Box/kit 4			
Eye shadows			
light pink	2.96	33.5	0.47
lemon green	13.5	1579	12.0
light blue	7.45	23.8	0.65
yellow	6.46	20.4	2.98
pink	3.89	33.5	0.57
lavender	4.0	28.7	0.54
violet	4.83	26.0	0.52
Lipsticks			
pink	<0.1	2.99	<0.2
light pink	2.35	5.05	<0.2
Lip gloss			
pink	<0.1	0.64	<0.2
red	<0.1	5.48	<0.2
lilac	<0.1	2.16	<0.2
Box/kit 5			
Lip balm/brown	<0.1	0.6	<0.2
Lip pencil/pink	1.41	1.69	0.48
Box/kit 6			
Lip gloss/all 7 colours[a]	<0.1	<0.1	<0.2
Box/kit 7			
Lip gloss/all 5 colours[b]	<0.1	<0.1	<0.2

[a]Dark silver, light silver, dark magenta, light magenta, dark orange, light orange, dark pink.

[b]Light pink, vermilion, glittery pink, glitter only, silver.

DISCUSSION

Paediatric allergic contact dermatitis (ACD) is a significant emerging problem. The reported prevalence of this condition varies greatly; values range from 5% to 70%, since patients with dermatitis in this age range are not routinely patch-tested. Non-homogeneous patients were enrolled in the studies and different series of allergens were applied (8–13). The incidence of ACD increases with age directly related to the exposure to environmental allergens (8–14).

Although recent studies have demonstrated that the prevalence of ACD in atopic and non-atopic patients is

Table II. *Number of samples containing amounts of nickel (Ni), chromium (Cr) and cobalt (Co) in 4 different ranges*

	Eye shadows ($n=29$)			Lipsticks ($n=5$)			Lip gloss ($n=15$)		
Quantity (ppm)	Ni	Cr	Co	Ni	Cr	Co	Ni	Cr	Co
>1000	0	3	0	0	0	0	0	0	0
>100≤1000	3	5	0	0	0	0	0	0	0
>10≤100	5	18	4	0	0	0	0	0	0
>1≤10	21	3	15	2	5	0	0	3	0

similar (9), atopic dermatitis is still considered a predisposing factor for ACD, because the damage to the epidermal barrier favours allergen penetration and because children with ACD are more exposed to sensitizers, which are present in the topical treatments necessary for their condition (10). The most common allergens causing sensitization in infants are nickel, chromium, cobalt, thimerosal and fragrances (14–17).

Several studies have demonstrated that adult patients with normal skin, previously sensitized to nickel, may develop contact dermatitis at concentrations of 5–10 ppm. On irritated skin, a concentration of 0.5 ppm is sufficient to trigger contact dermatitis (3, 18, 19).

Further dose-response studies in sensitized patients confirm that the minimum elicitation concentration is also approximately 1 ppm for chromium and cobalt (3); no studies have been performed to evaluate the threshold level of sensitization for nickel, chromium and cobalt in children.

As a consequence of the experimental studies, it has been widely agreed that cosmetic products should not contain more than 5 ppm of these metals. However, since an amount of nickel above 1 ppm can elicit contact dermatitis, the rule should be no more than 1 ppm (3, 18). As current regulation allows traces of nickel, chromium and cobalt in cosmetic products, these limits have become widely accepted in the literature.

A recent study carried out on a large number of adult eye shadows has shown that 75% of these products contained an amount of these metals over 5 ppm and that they all had a level above 1 ppm (20). However, the concentration never exceeded 50 ppm.

Nickel and cobalt amounts, respectively, above 13 and 9 ppm have been found when analysing other cosmetics (3).

These studies clearly demonstrate that, for consumers sensitized to metallic allergens, a risk of contact dermatitis elicitation exists when using cosmetic products. Furthermore, use of aggressive detergents or the presence of dermatoses that can damage the integrity of the skin barrier may increase penetration of allergens.

There is no literature on the presence of nickel, chromium and cobalt in toy cosmetics. Only one study examined fragrance allergens in toy make-up, revealing their unsafe presence (15).

The results of our study show that levels of over 5 ppm of nickel were present in 14 out of 52 (26.9%) samples of toy make-up; chromium exceeded 5 ppm in 28 out of 52 (53.8%) samples, with values over 1000 ppm in 3 eye shadows. For cobalt, 5 out of 52 (9.6%) samples contained amounts over 5 ppm.

Powdery toy make-up (eye shadows) contained the highest levels of metals, while "creamy" toy make-up (lip gloss and lipsticks) contained the lowest.

If toy make-up were regarded purely as a toy, it would have to meet the requirements of Directive 88/378 EEC (5). In our study, 4 kits did not conform to the safety rules because CE marking/certification was not present on their packaging, 2 of them reported no expiry date, and one did not declare the country of manufacture.

In conclusion, toy make-up should be considered a potential sensitizing agent. Particular attention should be paid in the case of atopic children with a damaged skin barrier. It should be emphasized that such "toys", which remain on children's most sensitive skin areas for hours, may not conform to the EEC Directive concerning the safety of toys.

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Table III. *Number of samples of toy make-up containing amounts of nickel, chromium and cobalt in the ranges less than 5 ppm and less than 1 ppm*

Toy make-up type (number of samples)	Metal (≤ 5 ppm)			Metal (≤1 ppm)		
	Nickel	Chromium	Cobalt	Nickel	Chromium	Cobalt
Eye shadows (29)	15/29	3/29	24/29	0/29	0/29	10/29
Lip gloss (15)	15/15	14/15	15/15	15/15	12/15	15/15
Lipsticks (5)	5/5	4/5	5/5	3/5	0/5	5/5
Lip balm (1)	1/1	1/1	1/1	1/1	1/1	1/1
Nail polish (1)	1/1	1/1	1/1	1/1	1/1	1/1
Lip pencil (1)	1/1	1/1	1/1	0/1	0/1	1/1

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