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Chemical safety of children's play paints: Focus on selected heavy metals

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ABSTRACT

Children's play paints are widely used as didactic products in preschool activities. Besides direct skin contact, a great risk of oral exposure exists during its normal and foreseeable use. Due to the ubiquitous nature of most metals, their presence as impurities in all products is recognized as unavoidable. However, the toxic potential of most of them requires that their levels are kept as low as possible.

The present study aimed to assess the content of selected heavy metals (Pb, Cd, Cr, Co, Ni, Mn, Cu and Zn) in "artist paints" (n = 54) and "face paints" (n = 12) commonly used in preschool establishments and available at low cost stores. Determinations were carried out by GFAAS (for Pb, Cd, Co, Cr and Ni) and FAAS (for Mn, Cu and Zn). The levels obtained [mean ± SD (maximum)] were: 0.48 ± 0.44 (1.98) μg g^{-1} for Pb; 0.04 ± 0.04 (0.30) μg g^{-1} for Cd; 0.17 ± 0.20 (1.47) μg g^{-1} for Co; 1.36 ± 2.18 (9.40) μg g^{-1} for Cr; 0.63 ± 0.56 (3.10) μg g^{-1} for Ni; 19.8 ± 88.2 (718) μg g^{-1} for Mn; 108 ± 260 (1458) μg g^{-1} for Cu; and 130 ± 564 (3478) μg g^{-1} for Zn.

A safety assessment considering the estimated potential exposure and health-based limits (tolerable daily intakes) was performed. Overall, the results showed no reasons for safety concerns regarding the studied elements.

1. Introduction

In early childhood education, activities such as drawing and painting help children to develop self-expression skills, and significantly contribute to their physical and psychological development [1]. According to Arda [2], painting is a stronger form of expression than words in early years, which makes play paints an attractive tool for preschool activities. These paints can be divided into two main groups: "artist paints" (e.g., gouaches, watercolors, acrylic paints) and the "face paints".

Given its purpose, *artist paints* fall within the concept of toy («a product designed or intended, whether or not exclusively, for use in play by children under 14 years of age») and their safety in the European Union is regulated under the Directive 2009/48/EC on the safety of toys (hereinafter the "Toy Safety Directive" will be designated as TSD) [3]. This category of toys is susceptible of easy ingestion in significant quantities and they should comply with maximum acceptable levels for the migration of toxic elements [4]. Metals may be released from toys by different mechanisms such as the action of saliva during mouthing, sweat during dermal contact or gastric fluid after ingestion [5]. Therefore, high amounts of metals may become bioavailable, reach the systemic circulation and exert their toxicological effects on target organs. Severity of the exposure depends on the content, physiological parameters, behavioral patterns and bioavailability of the metal [5]. The TSD lays down migration limits for 18 different elements, including the heavy metals Pb, Cd, Co, Cr, Ni, Mn, Cu and Zn.

As regards to *face paints*, they have to be considered as cosmetic products [«any substance or mixture intended to be placed in contact with the external parts of the human body (…) with a view exclusively or mainly to (…) changing their appearance…»], according to the EU Regulation (EC) no. 1223/2009 on cosmetics products (hereinafter "Cosmetics Regulation") [6]. The Cosmetics Regulation states that "products should be safe under normal or reasonable foreseeable conditions of use. In particular, a risk–benefit reasoning should not justify a risk to human health" [6]. Children's face paints are directly applied to the skin, and mainly produce local exposure to ingredients. However, the use of these products by children is of particular concern mainly because of the potential for exposure through ingestion [7].

The dermal contact with chemical substances, natural or synthetic, will always involve some risk of irritation and sensitization (particularly allergic contact dermatitis) [8–10]. Although topical exposure usually does not result in significant penetration through the skin, the human systemic exposure can rarely be completely excluded [8]. The risk of percutaneous absorption is variable depending on the site of application of the product (e.g., products applied directly to mucous membranes pose a greater risk). When children play with paints, skin contact and potential absorption through the skin are almost unavoidable.

Due to their ubiquitous and persistent nature, the presence of metals as impurities in all products is recognized as unavoidable (trace amounts arising from both the ingredients and manufacturing practices) [11]. However, for safety reasons, their levels should be kept at

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the lowest levels that are technically feasible or are of no toxicological concern.

Based on this background, the aim of our work was to determine the content of Pb, Cd, Cr (total), Co, Ni, Mn, Cu and Zn in artist paints and face paints used by children in preschool establishments and widely available in low cost stores. Results were compared with legal limits and values obtained in similar studies. It was also evaluated whether there were significant differences between metal content in the different types of products (gouaches, acrylics, watercolors, fingerpaints and face paints). In order to assess the safety of the products, the potential metal intake was evaluated and compared with tolerable daily intakes.

2. Material and methods

2.1. Sample collection

Using a convenience sampling procedure, samples of artist paints (n = 54) and face paints (n = 12) were collected in 8 preschool establishments (20 products) and purchased in 7 low cost stores (46 products) from Porto (Portugal). All the selected paints were specifically designed for children use, representing 17 popular brands. The paints collected in preschool establishments were mainly used by children aged between 3 and 6 years old. The general information about the samples (brand, type, color and country of manufacture) and the local of acquisition (school or store) is provided in Table 2. An identification code consisting of a combination of a letter and a number was assigned to each sample. For the artist paints the letters indicate the type of product: G — gouache; A — acrylic; W — watercolor; and FP — fingerpaint. Face paints are indicated by the letter "F". The brand is also indicated by a code consisting of a combination of a letter ("B", for brand) and a number. A different number was attributed to each sampling site too.

2.2. Sample analysis

The samples were solubilized by closed-vessel microwave-assisted acid digestion in a MLS-1200 Mega (Sorisole, Italy) microwave oven equipped with an HPR-1000/10 S rotor. A sample mass between 0.3–0.5 g was directly weighted into the microwave oven polytetrafluorethylene (PTFE) vessels and 4 mL of high-purity concentrated nitric acid (HNO_3) (65% w/w, *Trace*SELECT® Ultra, from Fluka, L'Isle d'Abeau Chesnes, France) plus 1 mL of high-purity hydrogen peroxide (H_2O_2) (30% v/v, *Trace*SELECT®, from Fluka, Seelze, Germany) was added. Then, the sample digestion was performed using the following microwave oven program (power [W]/time [min]): 250/2, 0/2, 600/5, 500/5, 400/5. After cooling, sample solutions were transferred into a 50 mL decontaminated polypropylene volumetric flask and the volume was adjusted with ultra-pure water (>18.2 MΩ.cm at 25 °C) obtained from a Milli-Q (Millipore, Billerica, MA) RG water purification system. Sample blanks were obtained using the same procedure. The obtained solutions (blanks and digested samples) were stored in tightly closed decontaminated polypropylene tubes in the refrigerator at 4 °C until analysis.

Each sample was analyzed in triplicate. The metal determinations were carried out using graphite furnace atomic absorption spectrometry (GFAAS) for Pb, Cd, Co, Cr and Ni, and flame-atomic absorption spectrometry (FAAS) for Mn, Cu and Zn.

For GFAAS determinations, a Perkin Elmer (Überlingen, Germany) model 4100 ZL instrument (longitudinal Zeeman-effect background correction), equipped with a transverse heated graphite atomizer (THGA) and an AS-70 auto-sampler was used. For FAAS determinations, a Perkin Elmer model 3100 instrument (air/acetylene flame) was used. Calibration standards were prepared by adequate dilution with HNO_3 0.2% (v/v) of a multi-element (Pb, Cd, Co, Cr, Ni, Mn, Cu and Zn) standard stock solution. This was prepared from single-element 1000 mg L^{-1} commercial standard solutions (Sigma, St. Louis, MO). The limits of detection (LoDs) were calculated as the concentration corresponding to 3 times the standard deviation of a series of 10 replicate measurements of the calibration blank (HNO_3 0.2% v/v).

2.3. Quality control

Since paints are not available as a certified reference material (CRM) for metal analysis, a sandy soil (ISE 918) supplied by WEPAL (Wageningen, The Netherlands) was used for analytical quality control purposes. The CRM was subjected to the same sample pretreatment as the studied paints. The values obtained proved the adequacy of the analytical procedure (Table 1).

The effect of the sample matrix on the accuracy of the analytical determinations was assessed through a matrix-matched calibration approach. Standard solutions were added to the matrix (i.e., paint), calibration curves were built and slopes were compared with those obtained for simple aqueous standard solutions. No significant differences ($p > 0.05$) were observed between the obtained slopes. Thus, the analytical procedures were considered free from matrix effects.

In each batch of microwave-assisted acid digestion (i.e., 10 vessels) one sample blank was included. In total, 23 sample blanks were performed. The obtained mean values were subtracted from the sample values.

2.4. Data analysis

Statistical analysis was performed using IBM (New York, NY) SPSS Statistics 20 software. For the statistics calculation, results that fall below the LoD were assumed as the LoD divided by the square root of 2, a commonly used procedure for data imputation [12]. Descriptive statistics was used to summarize the results for artist paints and face paints separately. Student's *t*-test was performed to evaluate the matrix effects. The difference in metal content between the different types of paints was tested with the non-parametric Kruskal–Wallis test followed by a multi-comparison analysis using the Dunnett's T3 test. Statistical significance was considered for $p < 0.05$.

2.5. Safety assessment

Measured metal content (Fig. 1) was used to assess the safety of the products using the methodology for assessment of chemical safety of toys, option 2 (use of product composition data), as proposed by the National Institute for Public Health and the Environment (RIVM) [13]. The exposure scenario considered was the direct ingestion, mostly associated with hand-to-mouth (HTM) contact. Hand-to-mouth contact is a child specific behavior that can lead to a relevant exposure [14], especially in children under 3 years of age. This methodology is based on the calculation of the amount of element released from the estimated amount of product ingested, i.e., the estimated daily intake (EDI) divided by the mean body weight of the children. This value should be lower than a defined fraction (usually 5, 10 or 20%) of the tolerable daily intake

Table 1
Results obtained from the CRM (sandy soil) analysis (mean ± SD; n = 3).

Element	Certified value (μg g^{-1})	Analytical value (μg g^{-1})	Recovery (%)
Cd	0.250 ± 0.030	0.237 ± 0.016	94.8 ± 6.4
Co	1.25 ± 0.20	1.23 ± 0.04	98.5 ± 3.3
Cr	25.3 ± 3.0	24.0 ± 0.8	95.0 ± 3.1
Cu	16.8 ± 0.8	16.0 ± 0.3	94.2 ± 4.7
Mn	173 ± 12.8	175.3 ± 2.3	101.4 ± 1.3
Ni	7.65 ± 0.70	8.00 ± 0.03	104.5 ± 3.9
Pb	21.6 ± 1.2	20.3 ± 1.0	94.2 ± 4.7
Zn	44.1 ± 3.3	43.6 ± 0.8	98.8 ± 1.8